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SOME DOUBLE SALTS OF LEAD.

BY JOHN WHITE.

Although it has long been known that the sulphate of lead is markedly soluble in aqueous solutions of the alkaline salts of certain organic acids, such as the acetates and tartrates of ammonium and sodium, it does not appear to have been generally remarked that this property of solubility applies also to other of the difficultly soluble lead salts.

During the course of some other work dealing with compounds of lead, it was observed that lead iodide dissolves to an appreciable extent in a concentrated aqueous solution of sodium acetate, yielding, upon evaporation, a white, crystalline crust, which was found to contain both lead and iodine. Subsequent experiments have shown that the chloride and bromide of lead behave like the iodide under similar conditions.

Upon search, it was found that the literature of the subject is very meagre, this property having been previously observed by only a few investigators, and that none of the text-books of chemistry make mention of the fact. The first authentic notice of it is contained in an article by Poggiale,[1] in which he describes a complex salt as being formed by heating to-

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[1] Ann. Chem. (Liebig), **56**, 234 (1845) ; Compt. rend., **20**, 1180.

gether lead chloride and basic lead acetate.   To this he gives
the formula $PbCl.5PbOC_2H_3O_2 + 15H_2O.$ The   published
data concerning this salt is such as to lead to the conclusion
that it was very impure.   Later, Carius[1] prepared a somewhat
similar compound by dissolving lead chloride in a water solu-
tion of lead acetate, to which he ascribes the formula

$$Pb \begin{cases} Cl \\ C_2H_3O_2 \end{cases} + Pb \begin{cases} C_2H_3O_2 \\ C_2H_3O_2 \end{cases} + 3H_2O.$$
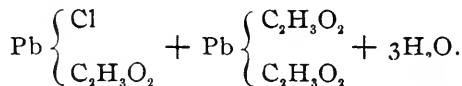
Judging from the description and the analyses, there is every
indication that his results and formula may be correct.   About
ten years later Tommasi,[2] apparently not being aware of the
work of Carius, succeeded in dissolving the iodide of lead in
a solution of potassium acetate, obtaining therefrom a crys-
talline compound to which he gave the formula

$$2Pb {\Large\diagup} \!\!\!\!\!\! \diagdown {}^{I}_{C_2H_3O_2} + KC_2H_3O_2.$$
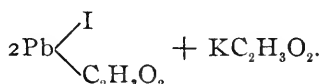
Later in this paper it will be seen that Tommasi probably had
a definite compound, although his formula does not agree fully
with the one there given.   In the same article he calls atten-
tion to the fact that the iodide is soluble to some extent in the
acetates of other bases, but he was unable to isolate any com-
pound which may have been formed, and concluded that they
acted as simple solvents.   Various other investigators have
observed somewhat similar behavior on the part of lead iodide,
among whom Nicklés[3] and Field[4] may be especially men-
tioned who did not, however, get at the true condition of re-
action.

The paucity of the literature upon the subject, and the un-
certainty of the results obtained, suggested the advisability of
undertaking a thorough investigation with the object of de-
termining the general character of this and allied reactions
and the nature and properties of the compounds, if any,

[1] Ann. Chem. (Liebig), **125,** 87 (1863).
[2] Ann. chim. phys. [4], **25,** 168 (1872) ; Bull. soc. chim., **17,** 337.
[3] Compt. rend., **56,** 388 (1863).
[4] J. Chem. Soc. (London), **26,** 575 (1873).

which are formed. Some of the results thus far obtained are recorded in the following pages.

The iodide was chosen as the most suitable of the halogen salts of lead to begin the experiments with, because decomposition of the resultant compound could be more readily detected by the change of color than if either the chloride or bromide were used. In the sequel this has proven to be the case, or, although the iodine compounds are less stable than the chlorine and bromine compounds, they are all white, or nearly so, whereas the decomposition-products are colored. This paper will deal only with the iodine compounds.

THEORETICAL.

Carius[1] describes the preparation of a class of compounds of the general formula $Pb\begin{cases} X \\ C_2H_3O_2 \end{cases}$, where X may be either chlorine, bromine, or iodine. To obtain these, he heated together in a sealed tube lead acetate and some alkyl halide, *e. g.*, ethyl, methyl, or methylene chloride. On heating to a proper temperature, reaction takes place, yielding an alkyl acetate and, what Carius calls, "*chloracetine of lead*," in a crystallized state. Schorlemmer[2] has prepared in a similar manner lead hexyl acetochloride, and in the course of this investigation a repetition of Carius' work has been carried out, substantiating his statements concerning the above compounds, with the exception of that containing iodine.

In attempting an explanation of the reaction, it would appear that we might apply to it the results obtained by von Ende[3] in his work upon the halogen salts of lead. He has shown that these salts dissociate into ions in two stages :

$$1. \ PbCl_2 = PbCl^{\cdot} + Cl' \ ;$$
$$2. \ PbCl^{\cdot} = Pb^{\cdot\cdot} + Cl'.$$
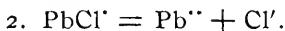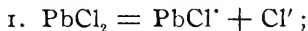
The first stage of ionization takes place much more readily than the second. It seems reasonable to suppose that other salts of bivalent lead dissociate likewise in two stages ; if so,

[1] *Loc. cit.*
[2] Ann. Chem. (Liebig), **199**, 142 (1879).
[3] Ztschr. anorg. Chem., **26**, 129 (1901).

the formation of compounds like $Pb{\displaystyle \diagdown_{C_2H_3O_2}^{Cl}}$ can be readily understood, for, supposing we start with the acetate, this would dissociate thus:

$$1. \quad Pb{\displaystyle \diagdown_{C_2H_3O_2}^{C_2H_3O_2}} = PbC_2H_3O_2{}^{\cdot} + C_2H_3O_2{}';$$

$$2. \quad PbC_2H_3O_2{}^{\cdot} = Pb^{\cdot\cdot} + C_2H_3O_2{}'.$$
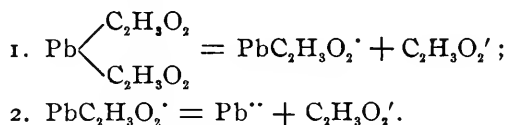
If, at the point represented by reaction 1, we imagine a halogen salt to be added, reaction would naturally take place between the positive ion $PbC_2H_3O_2{}^{\cdot}$ and the negative ion Cl', forming $Pb{\displaystyle \diagdown_{C_2H_3O_2}^{Cl}}$, a comparatively undissociated alkyl acetate being formed at the same time. The reverse reaction, *viz.*, that produced by the action of an alkyl acetate, *e. g.*, ethyl acetate upon lead chloride, ought to yield a similar product ; experiments have shown, however, that, because of the comparatively slight dissociation of the ethyl acetate and the very low degree of solubility of lead chloride in this, the reaction cannot be carried out in this way. To overcome the first objection, a metallic acetate was used instead of ethyl acetate, when it was found that, upon heating, a reaction does take place. It is to be presumed that the first product of this reaction is to form the compound $Pb{\displaystyle \diagdown_{C_2H_3O_2}^{X}}$. In reality, this compound has not been isolated in the case of the iodide, for the excess of the metallic acetate required to bring about a reaction is such as to carry it beyond this point, and there was always formed a compound of the general type,

$$\left(Pb{\displaystyle \diagdown_{C_2H_3O_2}^{X}} + M.C_2H_3O_2 \right),$$
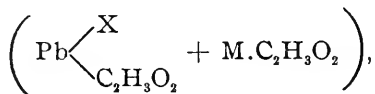
where X is any halogen and M any metal.

This formula has been written as a molecular compound, it being assumed that the acetoiodide of lead is formed as an inter-

mediate product. The method of formation and the decomposition of these compounds is in accord with this view, but further evidence is needed before this point can be accepted as proven.

<center>EXPERIMENTAL.</center>

As has been previously stated, the iodine salts are the ones to be described in this paper. These were found to be quite unstable, being easily split up by water and many other reagents. This behavior towards water probably furnishes an explanation for the fact that other investigators, notably Tommasi, were not more successful in isolating the salts formed, for, unless a large excess of the metallic acetate, and usually some acetic acid, be used in the water solution, lead iodide will either go over into a basic iodide, or, in case it goes into solution, the water is very apt to decompose the salt formed, precipitating out lead iodide again on cooling ; moreover, should a double salt be obtained, in washing it in order to remove the excess of acetate, just so soon as that excess is reduced beyond a certain amount decomposition would result, again yielding lead iodide.

This fact, which was noticed early in the investigation, suggested the necessity of using some other solvent than water, but this liquid must have a very considerable solvent power for the metallic acetate used, else it would not be possible to hold in solution a large enough excess to bring any of the lead iodide into solution, without at the same time diluting to such a degree that the solvent would exert a decomposing effect. Although alcohol, either strong, or, in some cases, diluted more or less with water, was found to be admirably adapted to the purpose, it was found that for certain acetates its solvent action is too slight, and salts containing these could not be prepared. It was further observed in using various solvents, that the degree to which the metallic acetate dissolves varies, and, therefore, to this extent, the solvent itself plays an important part in determining the exact composition of the salt formed. The reaction is, in fact, a very good illustration of the law of mass action. This phase of

the problem is now under investigation and the results will appear later.

The Acetoiodide of Lead.—In accordance with the statement made above, when lead iodide and a metallic acetate, such as sodium acetate, are brought together, there results a compound $Pb{<}^{I}_{C_2H_3O_2}$ $+ NaC_2H_3O_2$, it being assumed that the acetoiodide is formed as an intermediate product. If this view is correct, it ought to be possible to obtain the double salt through the interaction of the acetoiodide and the acetate. Attempts were, therefore, made to prepare the acetoiodide in order to test this. Carius[1] states that he obtained the acetoiodide by heating together in a sealed tube to 140° C. a mixture of 1 molecule ethyl iodide, slightly more than 1 molecule lead acetate, and 1 molecule acetic acid. All attempts so far made, following Carius' directions, to prepare the acetoiodide have failed. Frequently a small amount of a white, crystalline product could be observed in the tube, but invariably, while the reaction was still incomplete, decomposition set in, yielding large quantities of lead iodide in crystallized form. This precluded any possibility of securing the white substance in a condition fit either for use or analysis.[2] It was, therefore, not possible to carry out the experiment indicated above.

The Sodium Salt.—The first attempts to prepare the sodium salt were made by heating together in sealed tubes sodium acetate and lead iodide, using various liquids, *e. g.*, ethyl acetate, glacial acetic acid, alcohol, water, etc., as solvents. There was evidence of reaction in each case, and when a sufficient excess of sodium acetate was used, the lead iodide was entirely dissolved. Generally, a thin liquid, nearly colorless, was obtained, but when this was poured out of the tube it first solidified to a white, crystalline mass, then decomposed to form a yellow substance, the decomposition being accompanied by a

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[1] *Loc. cit.*, p. 89.

[2] Some more recent experiments, made just as this paper was being prepared for publication, indicate that, under somewhat different conditions, possibly the acetoiodide may be obtained.

marked evolution of heat. It was not possible to handle the crystals rapidly enough to secure them.

The above experiments having shown that a reaction takes place between the two substances, other methods were made use of for securing the products of the reaction. Finally, after considerable experimentation, the following method of preparation of the sodium salt was adopted : A rather concentrated solution of sodium acetate in (about 80 per cent) alcohol was prepared by the aid of heat. This was used as the solvent and to the boiling solution recently precipitated lead iodide was added in small portions at a time, until the solution became noticeably yellow. It was observed that the previous addition of a little glacial acetic acid, usually 2 to 5 cc., very materially increased both the amount of iodide which dissolves and the readiness with which it passes into solution. If the yellow solution, after filtering, be allowed to cool in the air marked decomposition ensues, but if, instead, the air be excluded this does not happen. To this end, the solution was cooled by placing the vessel containing it in a vacuum desiccator over concentrated sulphuric acid, the exhaustion being accomplished by means of a good water-pump, and set aside to crystallize. Under these conditions white, or nearly white, crystals could be obtained.

It was attempted to determine with some degree of certainty the proportions to be used in the preparation of the crystals, but no satisfactory results could be obtained. This was due in large measure to the instability of the salt, for it was found that the satisfactoriness of the preparation depended to a considerable extent upon the method of handling. Sometimes lead iodide, sometimes sodium acetate would separate out first, although apparently similar conditions had been observed. The salt itself is apparently more soluble in the mother-liquor than either of its constituents, and the excess of one or the other of these beyond a certain amount had to be removed before the double salt began to crystallize. The approximate quantities leading to the best results were : 40 to 50 grams sodium acetate in enough 80 per cent alcohol to make a moderately concentrated solution, 2 to 5 cc. glacial

acetic acid, and 10 to 12 grams lead iodide. From this solution, on cooling, no lead iodide separated, but several crops of crystallized sodium acetate were obtained which were removed as fast as formed. If, at any time, decomposition set in, the salt could always be brought into solution again by heating with the mother-liquor. After the separation of sodium acetate had practically ceased, the solution was again brought into the vacuum-desiccator and allowed to slowly evaporate, when large, almost white crystals were obtained.

It is easy to judge of the relative purity of the several crops of sodium acetate by[taking a portion of the salt, pressing out rapidly between drying-paper, then moistening with water or dilute acetic acid. Instant decomposition takes place, and since lead iodide is one of the products of the decomposition, the depth of color produced by this serves as a good qualitative test.

Several preparations of the salt were made and the crystals obtained were carefully examined each time under the microscope in order to determine if the tendency was to form a uniform product. This was found to be the case, except in one instance, to be noted[later.

The crystals consist of flat, orthorhombic plates, usually admixed with a small quantity of thin, pearly, white scales, from which they were separated mechanically, the large crystals being picked out. Crystals up to 3 by 1.5 to 2 mm. in diameter were obtained. The planes were well defined, but no measurements were made, the necessary apparatus not being at hand. The crystal form and the planes usually occurring are shown in the accompanying figure.

$a = \breve{P}n.$
$b = \infty \breve{P}n.$
$c = \infty \bar{P}\infty..$
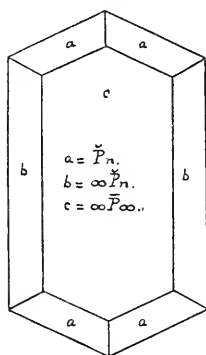
Fig. I.

To obtain the crystals in a form suitable for analysis, they were collected on a Witt filter and washed by the aid of the pump, with a wash liquid prepared by mixing together approximately equal volumes of anhydrous ethyl acetate and ordinary strong alcohol in which a small quantity of sodium

acetate had been dissolved. This precaution was found to be necessary in order to prevent (drive back) the dissociation of the double salt, which takes place as soon as most of the excess of sodium acetate has been washed out. After washing, the crystals were immediately transferred to a watch-glass, placed in the vacuum-desiccator, and dried in a vacuum over strong sulphuric acid. The yellowish tint can be removed by shaking the crystals in a stoppered flask with anhydrous ethyl acetate and letting them stand for twenty-four hours or longer, with occasional shaking. The salt becomes white and the liquid assumes a yellowish tint. This is not, however, necessary, as comparative analyses made with the pure white and the slightly yellow crystals showed that there was practically no difference in them. The color is probably due to a very slight superficial decomposition, with formation of lead iodide.

The analyses were made as follows : The iodine was determined by dissolving, by the aid of heat, in water slightly acidulated with nitric acid and precipitating the iodine as the silver salt. For the estimation of the lead and sodium, the solution in slightly acidulated water was saturated with hydrogen sulphide, precipitating out the lead as the sulphide. This, after filtering and drying, was transferred to a weighed porcelain crucible, and oxidized by fuming nitric acid, the excess of which was evaporated off. A drop or two of sulphuric acid was added, and this was then driven off by heating at a very low temperature over a free flame. The residue was ignited gently and weighed as sulphate. The filtrate was evaporated in a platinum dish on the water-bath, the slight trace of lead sulphide filtered out, and then the evaporation carried to dryness in a weighed platinum crucible, a few drops of concentrated sulphuric acid added, this fumed off, ammonium carbonate added, and the residue gently ignited, thus obtaining the sodium in the form of the sulphate. The results proved quite satisfactory. The carbon and hydrogen were determined in the usual way, by burning with lead chromate. Following are the results obtained :

0.5585 gram substance gave 0.3273 gram $PbSO_4$ and 0.0791 gram Na_2SO_4.

0.4078 gram substance gave 0.2396 gram $PbSO_4$ and 0.0590 gram Na_2SO_4.

0.3957 gram white substance gave 0.1821 gram AgI.

0.3762 gram of the same gave 0.1723 gram AgI.

0.6849 gram pale yellow substance gave 0.3143 gram AgI.

0.2494 gram substance gave 0.1032 gram CO_2 and 0.0364 gram H_2O.[1]

0.4424 gram substance lost, after heating four and a half hours, 0.0255 gram in weight.

0.2237 gram substance lost, after heating eight hours, 0.0133 gram in weight.

The analyses lead to the formula

$$Pb\!\!\bigg\langle{\!\!\begin{array}{l} I \\ C_2H_3O_2 \end{array}} + NaC_2H_3O_2.\tfrac{1}{2}C_2H_4O_2.$$
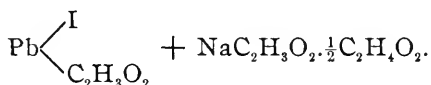
	Calculated for $PbNaI(C_2H_3O_2)_2.\tfrac{1}{2}C_2H_4O_2$.	I.	Found. II.
Pb	40.98	40.03	40.13
Na	4.57	4.59	4.69
I	25.12	24.86	24.76–24.79
C	11.89	11.28	....
H	1.60	1.64	....
$C_2H_4O_2$	5.95	5.76	5.95

The acetic acid of crystallization was determined by heating weighed portions of the pulverized substance in a double-walled vacuum air-bath, the heating liquid in the intermediate space being alcohol. Thus a temperature of 78° C., and, by means of a pump, a vacuum of 650 mm. was maintained. Under these conditions the acetic acid is driven off, about three hours sufficing to bring the substance to a constant weight. In one instance, after constant weight had been reached, water was substituted for alcohol in the bath and a further heating for three hours maintained at a temperature of 98° C., but without producing further loss of weight. If heated in the air, however, decomposition takes place rapidly, entailing a greater loss of weight. During the heating in a

[1] The second combustion was lost through an accident.

vacuum, the color changes from white to a pale sulphur-yellow ; in air the substance assumes a deep yellow color.

When heated in a melting-tube the substance changes to a pale yellow color at a temperature of about 90° C., between 95° and 100° it assumes an orange-red hue, and when still further heated it sinters at 120° and finally melts, with partial decomposition, to a reddish, syrupy liquid at 124° to 125° C. On cooling again it solidifies to a lemon-yellow, crystalline mass.

Up to the present no satisfactory solvent for the salt has been found. Water decomposes it instantly, yielding first lead iodide, later a basic iodide ; acids all produce decomposition with formation of lead iodide. It dissolves in hot alcohol, containing a considerable amount of sodium acetate, from which it can be again recovered. Alcohol alone, whether hot or cold, exerts no marked solvent action, but gradually produces decomposition. Anhydrous ethyl acetate is without effect, while hot benzene apparently dissolves it in small amount ; hot nitrobenzene dissolves it readily, but apparently there is a reaction other than that of solution between them. In dry air, as when kept in well-closed bottles, the salt is apparently perfectly stable, but if left exposed to the air under ordinary conditions it quickly turns yellow, the moisture in the air probably causing decomposition. Light is without appreciable action.

The statement was made above that, accompanying the coarse crystals in their formation, there was always another product, crystallizing in thin, pearly, white scales, and that in at least one instance the coarser crystals did not constitute the main portion of the product. In this case the thin flakes seemed to be chiefly produced. It was at first supposed that this was mainly sodium acetate, but, a qualitative test revealing the presence of too much lead iodide, it was decided to examine the substance more closely. The conditions for the formation of this product could not be determined, for although it is always a constituent of the product obtained from the action of sodium acetate upon lead iodide, it seems not to be the principal product. The one instance in which it was such

could not be duplicated, as no particular attention had been paid to the conditions under which that reaction was carried out. This salt was separated from the coarse crystals by taking advantage of the difference in specific gravity of the two. On shaking in a stoppered flask with ethyl acetate it was observed that the coarse granules settled rapidly, while this fine and specifically lighter substance remained for a long time in suspension, and by decantation the two could be separated. After a few such treatments, the heavier portion was found to contain 24.61 per cent of iodine, thus indicating that it consisted mainly of the salt first described. The lighter portion contained 18.34 per cent of iodine. The latter was subjected several times more to the treatment, when it was found that its iodine content had become constant. It was then dried and analyzed. Following are the results obtained :

0.4158 gram substance gave 0.1856 gram $PbSO_4$.

0.3477 gram substance gave 0.1559 gram $PbSO_4$.

0.4727 gram substance gave 0.1514 gram Na_2SO_4.

0.3477 gram substance gave 0.1109 gram Na_2SO_4.

0.5179 gram substance gave 0.1803 gram AgI.

After drying for seven hours at a temperature of 78° C., and with a vacuum reading of 650 mm., it was found that 0.5261 gram substance had lost 0.0236 gram in weight.

The most probable formula deduced from the analyses is

$$Pb\begin{cases} I \\ C_2H_3O_2 \end{cases} + 3NaC_2H_3O_2.\tfrac{1}{2}C_2H_4O_2.$$

	Calculated for $PbNa_3I(C_2H_3O_2)_4.\tfrac{1}{2}C_2H_4O_2$.	I.	II.
			Found.
Pb	30.93	30.48	30.62
Na	10.34	10.39	10.35
I	18.96	....	18.81
$C_2H_4O_2$	4.49	4.49	....

Although the method of purification leaves room for doubt if this be really a definite substance or a mixture of the other salt with sodium acetate, the appearance of the substance and the uniformity and close agreement of the analytical results with the calculated values for the above

compound would seem to indicate that it is in all proba-
bility a new salt.   If we are right in supposing this whole
class of compounds to be formed by molecular union (if the
word has any significance), then it is possible to imagine
the existence of a whole series of such compounds.   It has
already been stated (p. 5) that certain recent results ob-
tained under different conditions lead also to this conclusion.

The Potassium Salt.—As stated in the introduction, Tom-
masi,[1] in his work, obtained a potassium lead acetoiodide, to
which he gave the formula $2Pb\begin{smallmatrix}I\\C_2H_3O_2\end{smallmatrix} + KC_2H_3O_2$.   This
substance he prepared by dissolving 1 molecule lead iodide in
a hot aqueous solution of potassium acetate, containing 2
molecules.   This, on cooling, deposited a pale-yellow, crys-
talline mass, which he redissolved by heating with twelve
times its weight of absolute alcohol and allowed to cool in a
desiccator over lime.   In this way he obtained a large quan-
tity of white crystal flakes.   There are no analytical results
given in the article, and although the formula ascribed to the
substance by Tommasi differs from that which we shall use,
the general appearance and properties, as well as the methods
employed in the preparation of Tommasi's salt are so nearly
similar to ours as to leave but little room for doubt that they
are identical but that his formula is probably incorrect.

The potassium salt is much easier of preparation than the
sodium compound, but harder to purify.   It is easier to pre-
pare because it is very much less soluble in the mother-liquor
and much more stable towards reagents than the sodium salt.
Instead of using strong alcohol as solvent a quite dilute, al-
most 50 per cent, alcohol may be used.   Indeed lead iodide
will dissolve to a greater extent in the more dilute alcoholic
solution of the acetate.   To prepare the salt, make a fairly
concentrated solution of potassium acetate in 50 to 60 per cent
alcohol—acetic acid need not be added, for its presence seems
in this case to be harmful ; in the boiling solution lead iodide
was dissolved in small portions at a time until the solution was

Loc. cit.

practically saturated and no more would dissolve without long-continued heating. The cooling of the solution was carried out in a partial vacuum and generally did not proceed far before precipitation began ; the mass finally became almost solid. This was redissolved by adding more alcohol and heating. From this solution beautiful, pearly-white leaflets precipitated out on cooling. For washing these an alcohol-ethyl acetate mixture was used, containing 2 to 3 per cent potassium acetate. Owing to the tendency of the crystal flakes to pack on the filter, and further, to decompose while moist, it was nearly impossible to get the salt thoroughly washed. The analyses show the presence of potassium acetate as an impurity. The drying was accomplished in the same manner as with the sodium salt and the analyses were carried out in a similar manner. The following results were obtained :

0.2463 gram substance gave 0.1494 gram $PbSO_4$ and 0.0517 gram K_2SO_4.

0.2888 gram substance gave 0.1760 gram $PbSO_4$.

0.4028 gram substance gave 0.0811 gram K_2SO_4.

0.2795 gram substance gave 0.1355 gram AgI.

0.3010 gram substance gave 0.1436 gram AgI.

A second preparation gave :

0.2868[1] gram substance gave 0.1743 gram $PbSO_4$.

0.4422[1] gram substance gave 0.2686 gram $PbSO_4$.

0.3862 gram substance gave 0.0799 gram K_2SO_4.

0.2591 gram substance gave 0.1235 gram AgI.

0.4211[1] gram substance gave 0.1648 gram CO_2 and 0.0464 gram H_2O.

0.3727[1] gram substance gave 0.1463 gram CO_2 and 0.0409 gram H_2O.

The formula deduced from the above results is
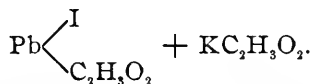
$$Pb\underset{C_2H_3O_2}{\overset{I}{\diagdown}} + KC_2H_3O_2.$$

	Calculated for $PbKI(C_2H_3O_2)_2$.	Preparation A. I.	Preparation A. II.	Found. Preparation B. I.	Preparation B. II.
Pb	42.14	41.42	41.62	41.50	41.48
K	7.97	9.43	9.50	9.29	....
I	25.84	25.81	25.78	25.75	....
C	9.77	....	....	10.67	10.71
H	1.23	....	....	1.21	1.23

Some adhering potassium acetate probably is the occasion for the high values for potassium and carbon and the slightly low value for lead, though these may be due to an inherent error in the method of analysis used.

The heating in the vacuum-oven produced no change in weight, and showed that the salt contained no acetic acid. The same was found to be the case with one sample in which acetic acid had been used in the preparation.

When heated in a melting-tube, no change was observed up to 205° C., when the substance showed signs of sintering and turned only slightly yellow. At 208° to 208°.5 C., it melted fairly sharply to a pale, straw-colored liquid, which solidified on cooling to a white, crystalline mass, which again gave the same melting-point, thus proving that no decomposition had taken place.

From the mother-liquor, after removal of the potassium salt, there was obtained, upon evaporation, a crop of white, crystal needles, which readily turned slightly yellow on standing. The appearance and properties of this product are very closely in accord with those of the double iodide of lead and potassium described by Remsen and Herty[1] and by Wells.[2] A product which had not been specially purified gave 54.30 per cent iodine, whereas $KPbI_3.2H_2O$ requires 57.46 per cent.

The Ammonium Salt.—This was prepared in the same way as the sodium salt, except that no acetic acid was necessary, the reaction working better without it. The ammonium salt is so insoluble that it was frequently precipitated from the boiling solution, and differs from both the sodium and potassium salts in that it is not soluble in the mother-liquor on

[1] This JOURNAL, 11, 296; *Ibid.*, 14, 107.
[2] Am. J. Sci., 45, February No. (1903); "Studies from the Chemical Laboratory of Sheffield Scientific School, Yale University," Vol. I., p. 250.

heating. On account of the tendency to precipitate from the hot solution, the conditions of preparation can be varied between tolerably wide limits without affecting the nature of the product. A number of preparations was made, the same white, highly-crystalline product being obtained in each case. The method of washing and purification used was the same as for the sodium and potassium compounds. The salt is very unstable, decomposing very readily in air, especially while in the moist condition. Light also produces decomposition, so that the salt had to be protected from its action.

Generally, the product obtained was in the form of a fine, crystalline powder, but in a few instances fairly large, 1 to 2 mm. crystals were obtained. These showed very perfect crystal form, the planes being well defined. The crystals were apparently orthorhombic prisms, the accompanying figure showing the more common type.

$a = OP$.
$b = \infty \breve{P} \infty$.
$c = \infty \breve{P} \infty$.
$d = \infty \breve{P} n$.
$e = \breve{P} \infty$.
$f = \breve{P} \infty$.
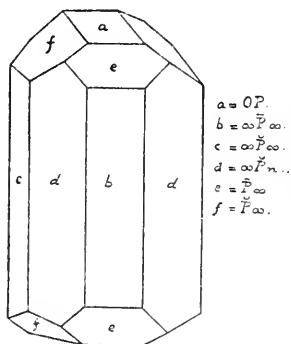
Fig. II.

In making the analyses, the methods used were the same as those previously described, except that instead of precipitating the lead as sulphide the substance was treated directly with concentrated sulphuric acid, which was fumed off and the lead thus obtained directly as sulphate. The ammonia was only tested for qualitatively, the small amount of substance at hand making a quantitative estimation somewhat uncertain. Three different preparations were analyzed, designated below as A, B, and C, respectively. The following are the results obtained :

A. 0.4639 gram substance gave 0.2327 gram AgI.

B. 0.2873 gram substance gave 0.1430 gram AgI.
   0.2492 gram substance gave 0.1257 gram AgI.
   0.3501 gram substance gave 0.1748 gram AgI.
   0.3535 gram substance gave 0.1761 gram AgI.
   0.2774 gram substance gave 0.1788 gram $PbSO_4$.

C. 0.1948 gram substance gave 0.1254 gram $PbSO_4$.

0.2583 gram substance gave 0.1669 gram $PbSO_4$.

0.2996 gram substance gave 0.1506 gram AgI.

The formula deduced from the analyses is

$$Pb\Big\langle{}^{I}_{C_2H_3O_2} + NH_4C_2H_3O_2.$$
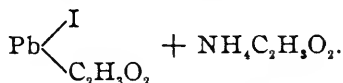
	Calculated for $PbNH_4I(C_2H_3O_2)_2$.	A.	Found. B.	C.
Pb	44.03	....	44.02	43.96–44.12
I	27.00	27.10	26.89–27.25–26.98–26.91	27.16

Heat causes decomposition with loss of ammonia and acetic acid, leaving lead iodide. When heated in a melting-tube the salt rapidly turns to a deep lemon color, sinters at about 157° C., and melts to an amber-colored liquid at 166° to 167° C. The liquid does not again solidify unless considerably super-cooled, when it forms a solid resembling lead iodide.

On evaporating the mother-liquor there was obtained a considerable quantity of long, slender, hair-like needles, forming tufts radiating from a common center. While in the solution these are pure white, but change in color so rapidly when taken out that it was impossible to obtain them in the dry state except as pale, sulphur-yellow crystals. They are extremely sensitive to light. Some of the powdered substance exposed to the action of diffused sunlight turned first yellow then brownish-red. Direct sunlight transforms this into a grayish-brown color, with liberation of iodine. The appearance and properties of the substance so strongly suggested the double ammonium lead iodide described by Wells[1] that an analysis was made, with the following results :

0.1430 gram substance gave 0.0678 gram $PbSO_4$.

0.1611 gram substance gave 0.0766 gram $PbSO_4$.

0.1402 gram substance gave 0.1512 gram AgI.

0.1374 gram substance gave 0.1476 gram AgI.

	Calculated for $NH_4PbI_3.2H_2O$.	Found. I.	II.
Pb	32.24	32.38	32.48
I	59.36	58.27	58.04

[1] Am. J. Sci., **46**, July No. (1893) ; "Sheffield Scientific Studies, Yale University," Vol. I., p. 283.

The analysis confirms the supposition that this is a double iodide. When the needles are shaken up with alcohol containing ammonium acetate they immediately dissolve, and from the solution ammonium lead acetoiodide was obtained upon evaporation.

The formation of the above salt as a by-product of the action of ammonium acetate on lead iodide, and of a similar potassium lead compound formed under similar conditions, may be taken as evidence bearing upon the general character of the reaction, showing that at least a partial exchange between the two salts has taken place.

The Lead Salt.—In his paper dealing with the salts of the type $Pb\begin{smallmatrix}Cl\\C_2H_3O_2\end{smallmatrix}$, Carius[1] observes that this is decomposed by water, a white powder being first thrown out which, however, soon goes into solution ; further, that the lead halides are soluble in lead acetate solution, and that in both instances the same double salt is formed. To this, based upon a chlorine estimation, he gives the formula

$$Pb\diagdown^{Cl}_{C_2H_3O_2} + Pb(C_2H_3O_2)_2.3H_2O,$$
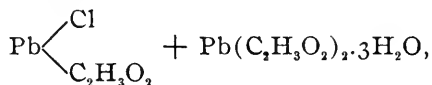
and therefore a salt of the same type as those previously described in this paper. Although Carius mentions the fact that lead iodide acts like the chloride under similar conditions, he apparently did not isolate the double salt, as no description of it is given. It is doubtful if he prepared the salt at all, for a repetition of his work reveals the fact that when lead iodide is dissolved in a water solution of lead acetate practically the whole of it is converted into basic iodide. The same is indeed the case when an alcoholic solution of the acetate is used, unless a relatively large amount of acetic acid is added.

The iodide of lead is not so readily soluble in lead acetate solution as in solutions of the alkaline acetates. The following proportions, used in several instances with good success,

[1] *Loc. cit.*

will give an idea of the solubility : Fifty grams lead acetate
in solution in 100 cc. 93 per cent alcohol and 30 cc. glacial
acetic acid, dissolved at the boiling temperature approxi-
mately 4 grams lead iodide ; an equal amount of sodium ace-
tate will dissolve 25 grams of the iodide. The solution in
lead acetate does not have to be cooled in a partial vacuum,
as it exhibits but small tendency to decompose so long as it is
in contact with the acetate solution. The salt obtained was
well crystallized, forming well-defined, monoclinic prisms.
The forms most frequently observed are shown in the accom-
panying figure. Occasionally, well-defined, interpenetration
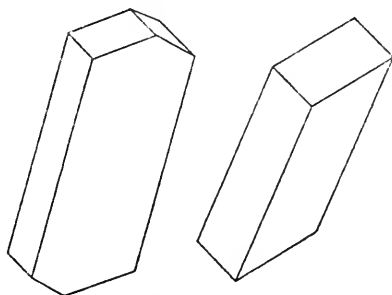
Fig. III.

twins were obtained, the individuals being arranged at right
angles in the form of a Latin cross. The washing of the crys-
tals is most readily accomplished by decantation, after shaking
or stirring with absolute alcohol containing a trace of lead
acetate, the final washing being carried out on a Witt filter
by aid of the pump. The crystals were then dried in a
vacuum over sulphuric acid. They are stable in dry air, but
are decomposed by water and other reagents. The analyses
were made in the same manner as with the ammonium salt
and gave the following results, two samples being analyzed :

A. 0.1447 gram substance gave 0.1201 gram $PbSO_4$.

0.1279 gram substance gave 0.1055 gram $PbSO_4$.

0.2620 gram substance gave 0.0792 gram AgI.

After a further washing, the same substance gave :

0.3134 gram substance gave 0.0960 gram $PbSO_4$.

0.1523 gram substance gave 0.1263 gram AgI.

B. 0.1096 gram substance gave 0.0907 gram AgI.

0.1074 gram substance gave 0.0333 gram $PbSO_4$.

0.7587[1] gram substance gave 0.2866 gram CO_2 and 0.1024 gram H_2O.

0.3256[1] gram substance gave 0.1259 gram CO_2 and 0.0424 gram H_2O.

On heating in a vacuum-bath at 77° C., the substance rapidly lost in weight up to a certain point, after which a very slow further loss was observed. 0.8712 gram lost 0.0327 gram. This corresponds very closely to the calculated loss required by the formula given. All compounds containing lead acetate show this gradual loss, probably caused by decomposition.

The analyses indicate the formula

$$Pb{<}^{I}_{C_2H_3O_2} + Pb{<}^{C_2H_3O_2}_{C_2H_3O_2}.\tfrac{1}{2}C_2H_4O_2.$$
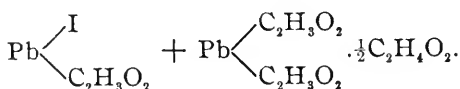
	Calculated for $Pb_2I(C_2H_3O_2)_3.\frac{1}{2}C_2H_4O_2$.	Found.	
		A.	B.
Pb	55.34	56.67–56.63–56.51	56.33
I	16.96	16.33–16.55	16.75
C	11.23	....	10.31–10.54
H	1.48	....	1.51–1.46
$C_2H_4O_2$	4.01	3.75+	....

When the salt was heated in a melting-tube it assumed a slight yellowish tint with signs of sintering at about 180° C.; at 192° it became pasty and melted slowly to a clear amber-colored, very viscous liquid at 202° to 205° C. No visible decomposition took place during the heating.

The Action of Solvents.—It has been stated that most of the substances commonly employed as solvents exert a decomposing action upon the double acetoiodides. This is especially the case with water, the alcohols, and the acids, while anhydrous ethereal salts and hydrocarbons seem to have little or no action. In consequence of this it has not been possible to determine the molecular weights of the salts and thus test the correctness of the formulas given. The decomposi-

[1] These analyses were made for me by Miss Fossler.

tion-products produced by water and alcohol were studied, however, with the idea of obtaining additional evidence bearing upon the structure. For this purpose the sodium, potassium, and ammonium salts were pulverized and shaken up in stoppered flasks with water and with absolute (96 to 98 per cent) alcohol, respectively, the time of extraction varying from 24 hours to six days.

In each instance the action of water was to produce an almost instantaneous decomposition, yielding lead iodide, shown by the orange-yellow color characteristic of this substance in the amorphous state. In a short time, however, the color began to change, turning much lighter in hue. This change proceeds very slowly, the time required for its completion varying with the size of the particles and with the individual salt, the potassium salt usually reacting more slowly than the others. At the end the color was a light sulphur-yellow. The following analyses of the residues obtained from the sodium, potassium, and ammonium salts—designated in the table as A, B, and C, respectively—show that this is a basic iodide :

	Calculated for PbI(OH).	A.	Found. B.	C.
Pb	58.98	58.58	....	58.97
I	36.16	36.44	36.13–36.21	36.16

The action of absolute alcohol upon the three double salts was, in general, of a character similar to that of water, but in this instance the nature of the individual salt seemed to play an important rôle, for it was found that the potassium salt, which is easiest of the three to prepare, showed almost no action with alcohol, there being scarcely any change in color even after several days digestion, and an iodine estimation gave 25.74 per cent iodine, the original salt containing 25.84 per cent, thus showing that no decomposition had resulted. The ammonium salt, which stands next to the potassium salt in ease of preparation, showed, after an equal time of digestion, a slight decomposition. The residue gave 30.73 per cent iodine, while the original salt contains 27 per cent. The decomposition in the case of the sodium salt was almost

complete, giving 33.64 per cent of iodine, while the original salt contained 25.12 per cent and the basic iodide 36.16 per cent.

It appears as if there were a tendency to reach a state of equilibrium, for in several instances, although the time of digestion varied, the composition of the residue was the same. This point has not yet been thoroughly tested.

A study of these decomposition reactions suggests that the first action of the solvent is to split up the double salt into its components :

$$1. \left(Pb {<}^{I}_{C_2H_3O_2} + M.C_2H_3O_2 \right) = Pb{<}^{I}_{C_2H_3O_2} + M.C_2H_3O_2.$$
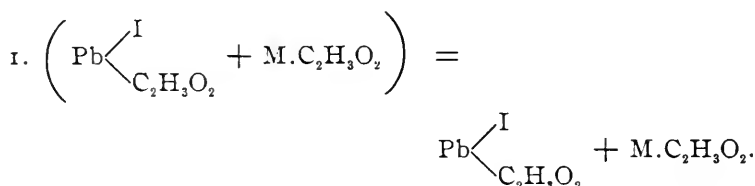
This reaction will proceed more or less slowly according to the degree of solubility of the double salt and of the metallic acetate formed. Subsequent to this a second reaction takes place, yielding lead iodide :

$$2. \ 2Pb{<}^{I}_{C_2H_3O_2} = PbI_2 + Pb(C_2H_3O_2)_2.$$
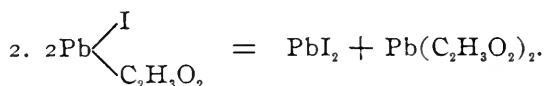
It is not quite so easy to follow the reactions involved in the formation of the basic iodide. There are two possible ways in which it could be regarded, *e. g.* :

$$a. \ PbI_2 + H_2O = PbI(OH) + HI ;$$

$$b. \ Pb{<}^{I}_{C_2H_3O_2} + H_2O = PbI(OH) + H.C_2H_3O_2.$$
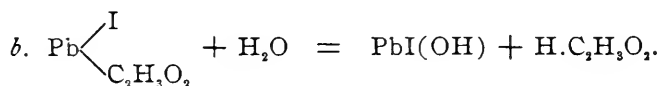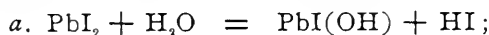
If the first of these is correct, the presence of iodide in the filtrate ought to be possible of detection. As a matter of fact, tests show only such traces of these as can be accounted for from the solubility of lead iodide. It ought further to be possible to transform freshly precipitated lead iodide into the basic salt by the action of water. Experiment shows that neither cold nor hot water has this effect to any extent.

Reaction *b* can be regarded as true only by assuming that reaction 2 above is reversible, for there can be no doubt that the first action of water is to yield lead iodide, which can only be transformed into the basic iodide by supposing that the reaction first reverses itself and then the acetoiodide formed is acted upon by water in the sense indicated in reaction *b*. Assuming this to be correct, reaction 2 should be written

$$2Pb{\diagdown \begin{smallmatrix} I \\ C_2H_3O_2 \end{smallmatrix}} \;\; \overset{\longrightarrow}{\longleftarrow} \;\; PbI_2 + Pb(C_2H_3O_2)_2.$$
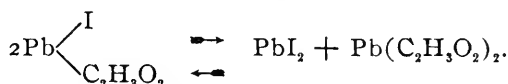
This reaction would take place at first very readily in the sense from left to right on account of the instability of the acetoiodide and the insolubility of the lead iodide. The conversion, however, of the iodide into the less soluble basic iodide would proceed much more slowly because of the insolubility of the iodide and the small active mass of the lead acetate. It was found that the addition of lead acetate very materially hastened the conversion into the basic salt. Indeed it was found easily possible to transform freshly precipitated lead iodide into basic iodide by shaking with cold water containing a considerable excess of lead acetate. Other acetates produce a like result, but less readily, indicating that, in all probability, lead acetate must be first formed. These experiments all tend to show the reversibility of the above reactions. That reaction *b* takes place is indicated by the presence of acetic acid in the filtrate, which was easily proven. An addition of acetic acid should have the tendency to prevent this. Experiments carried out in strong alcohol indicated the correctness of the supposition, for an excess of acetic acid prevented the conversion of the iodide into basic iodide. It was found, however, that if the glacial acetic acid used be added in small quantities at a time and thoroughly mixed by shaking, a very considerable amount could be added without preventing the formation of the basic iodide. This was to be expected, for the dissociation of the acid is so slight in comparison with that of its salts that a large excess of it would be needed to counteract the influence of the lead acetate in causing reaction 2 to reverse itself.

The above discussion is based upon the primary assumption that the double salts are to be regarded as molecular compounds, containing the molecule $Pb\big\langle\begin{smallmatrix} I \\ C_2H_3O_2 \end{smallmatrix}$. The observed facts are so well in accord with this, that, taken in conjunction with the methods of formation, they indicate the strong probability of the correctness of the assumption. It is hoped that, by the preparation of the acetoiodide, additional evidence may be obtained bearing upon this point, which cannot yet be regarded as fully established. The investigation is still in progress and it is hoped that this evidence may be soon forthcoming.

Univ. of Nebraska,
Lincoln, June, 1903.

A FURTHER INVESTIGATION OF PARATOLUENE-DIAZONIUM SULPHATE AND OF THE ACTION OF SULPHURIC ACID ON THE METHYL ETHER OF PARA-CRESOL.[1]

By Gellert Alleman.

This investigation is in part a continuation of one by Chamberlain, the results of which have already been published.[2] Chamberlain found that by decomposing paratoluenediazonium nitrate or sulphate with methyl alcohol under ordinary atmospheric pressure, as well as under diminished or increased pressure, both paramethoxytoluene and toluene were formed. He also confirmed the observation of Remsen and Dashiell[3] that lowering the pressure favors the hydrogen reaction in the case of the nitrate.

Preparation of Paratoluenediazonium Sulphate.

One hundred grams of paratoluidine were placed in an Er-

[2] This Journal, 19, 531.

[3] *Ibid.*, 15, 301.

lenmeyer flask of 1 liter capacity, and 500 grams of anhy-drous methyl alcohol added.   As soon as complete solution took place 100 grams concentrated sulphuric acid were added by means of a dropping-funnel, allowing only a few drops into the flask at one time.   Even with the slow addition of the acid and constant shaking of the flask, it was found necessary to place the flask in cold water to prevent loss of the alcohol on account of the heat generated by the reaction.   As soon as a slight excess of sulphuric acid is added, the precipitate of paratoluidine sulphate which first separates goes into solution and does not again appear when the flask is placed in water containing ice.

The flask is then surrounded by ice-water and a rapid cur-rent of nitrous fumes passed through the solution for about thirty minutes.   The fumes were cooled before being con-ducted into the vessel by first passing them through two gas bottles which were placed in cold water.   After a time, crys-tals of paratoluenediazonium sulphate appear in the flask. They have a red color, but on being washed with ether the color disappears, showing the crystals to be glistening, snow-white flakes.   The fumes are conducted through the solution till a few drops of the removed liquid, on treatment with dilute caustic soda, no longer give the odor of paratoluidine.

The diazo compound, when dry, is a comparatively stable body.   Crystals were kept in a desiccator for six weeks with-out the least evidence of decomposition.   If the crystals are filtered off and the filtrate is allowed to stand in a cool place, perfectly transparent, almost colorless prisms crystallize from the solution.

Decomposition of the Diazonium Compound with Methyl Alcohol.

Instead of taking the crystals of the diazonium sulphate out of the flask and purifying them by washing with ether and then effecting the decomposition, as is usually done in analogous cases, the flask was provided with a return-con-denser and placed on a water-bath.   Decomposition began at the ordinary temperature, but it was slight.   At about 60° the

decomposition was rapid and the reaction had to be checked at times by pouring cold water on the outside of the flask. After the evolution of gas had almost ceased, the temperature was raised and the liquid boiled rapidly for twenty minutes in order to make sure that the decomposition was complete.

It will be seen from the above statements that the decomposition was effected in the presence of all those compounds which were formed in the flask during the diazotizing process.

Separation and Purification of the Methyl Ether of Paracresol.

After it was judged that the decomposition had been completely effected, several portions were placed in a large balloon flask provided with a Hempel tube about 3 feet high. The methyl alcohol was then distilled and some toluene came over with it, showing that the hydrogen reaction had also taken place. When the distillation was conducted too fast it was found that some of the oil came over with the alcohol. As soon as the thermometer at the top of the Hempel tube rose above 64° the distillation was discontinued and, after the solution had cooled somewhat, water was added to the flask. The distillation was then continued and quite a quantity of methyl alcohol passed over, showing that methyl sulphuric acid was, in all probability, formed, and that it broke down on the addition of water. After the methyl alcohol was removed as completely as possible by this method, the contents still remaining were treated with about twice the volume of water. The flask was then connected with a condenser, placed on a sand-bath, and heated almost to the boiling-point of the liquid contained in it. On passing steam through the mixture, a yellow oil came over with the distillate. This oil has an extremely great surface-tension. When nearly all of the oil had passed over it was noticed that the last portions were of a red color. The oil was then separated by means of a separating-funnel, dried with calcium chloride, placed in a distilling-bulb, and, after several distillations, a product was obtained which boiled at 174° to 176°. This is the methyl ether of paracresol described by Körner,[1] and also obtained

[1] Ztschr. Chem., 1868, p. 326.

by Chamberlain,[1] who gives its boiling-point as 174°.5 (corr.). Its identity was established by the formation of anisic acid when it was oxidized by potassium permanganate.

It was thought that probably the oil which came over above 180° might have its boiling-point raised by the presence of nitro-compounds and for the purpose of removing the latter, in case they were present, the whole portion of the high-boiling oil was treated with granulated tin and hydrochloric acid. After treatment in this manner it was washed repeatedly with water and finally dried with calcium chloride. It was then distilled and nearly the entire portion passed over between 174° and 176°, showing that the rise in the boiling-point of a portion of the oil was undoubtedly due to the influence of nitro-compounds which can be removed by the well-known method above described.

The tar which remained in the flask into which steam had been passed was dissolved in alcohol and the alcohol slowly evaporated, but no crystals were obtained. It was then treated with ligroin, from which yellow needles separated. These needles melted at 74° to 79°. Chamberlain investigated this tarry material, and found that it contained dinitropara-cresol, $(CH_3.NO_2.OH.NO_21 : 3 : 4 : 5)$. He found the melting-point of this substance to be 80°.5 (corr.), and accounts for its formation by the fact that nitric acid is formed in the flask and acts on the paramethoxytoluene. He obtained the dinitroparacresol by the treatment of the methyl ether of paracresol with strong nitric acid and glacial acetic acid.

Action of Sulphuric Acid on Paramethoxytoluene.

The paramethoxytoluene was poured into pure concentrated sulphuric acid contained in an Erlenmeyer flask. The proportions in which the two compounds were brought together were 3 grams of sulphuric acid to 1 gram of para-methoxytoluene. The mixture assumed a dark-red color and became warm, indicating that some action took place at the ordinary temperature. The flask was placed on a water-bath and heated till a few drops of its contents dissolved in water

[1] *Loc. cit.*

without cloudiness, showing that the paramethoxytoluene had been completely transformed into a sulphonic acid. On cooling, part of the sulphonic acid separated as yellow crystals.

The sulphonic acid was converted into the barium salt re-repeatedly. This is a pure white, semi-crystalline material, very soluble in cold water, and insoluble in alcohol. Attempts to obtain definite crystals by crystallizing the salt under different conditions of concentration gave negative results.

Preparation of Paramethoxymetatoluenesulphonic Acid.

The acid was separated by adding to the aqueous solution of the barium salt above described sufficient dilute sulphuric acid to exactly precipitate the barium. The acid is extremely soluble in water—one part dissolving in about half its weight of water. It is almost insoluble in ether, benzene, and ligroin, but dissolves readily in methyl and ethyl alcohol and hot acetone. From water it separates at first in the form of yellow, flaked crystals. The color can be removed by washing the acid with cold anhydrous ether. If, after treatment in this way, it is crystallized from alcohol, perfectly colorless, long prisms can be obtained, which melt at $105°$ to $108°$. The prisms have a hexagonal shape.

Sodium Salt, $C_6H_3 \diagup^{CH_3}_{\diagdown OCH_3} - SO_2ONa + \frac{1}{2}H_2O.$ —This salt was made
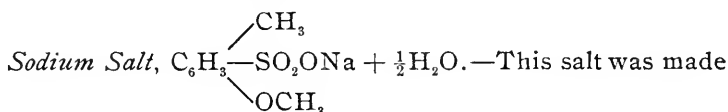
by exactly neutralizing an aqueous solution of the free sulphonic acid by means of sodium carbonate. The salt at first crystallized in small, orange-colored needles. Upon recrystallizing, colorless prisms were obtained. If allowed to stand in the air any length of time they effloresce.

Another sodium salt was prepared by exactly precipitating the barium, in an aqueous solution of the barium salt, by means of a dilute solution of sodium sulphate. After filtering off the barium sulphate and evaporating the solution to a small volume, perfectly transparent, colorless needles separa-

ted. These, on exposure to the air, also lost water and turned white.

Analyses show that both of the salts prepared as described above are identical in their composition. They are insoluble in strong, boiling alcohol. Estimations of sodium and water gave the following results:

	Calculated for $C_6H_3\overset{CH_3}{\underset{OCH_3}{-}}SO_3Na + \frac{1}{2}H_2O.$	Found.			
		Salt from free acid.		Salt from Ba salt.	
		I.	II.	III.	IV.
H_2O	3.86	3.96	3.98	3.89	3.92
Na	9.87	9.88	9.72	10.04	10.07

Potassium Salt, $C_6H_3\overset{CH_3}{\underset{OCH_3}{-}}SO_2OK + 2H_2O.$—A hot solution of the free sulphonic acid was carefully neutralized with pure potassium carbonate. Transparent, slightly red needles were first obtained, and, on recrystallizing these, large prisms, which had a slight yellow color, separated. The salt was purified by boiling it with 50 per cent alcohol, from which it crystallizes, when the solution is concentrated, in colorless needles, which radiate from the central point; from dilute solutions, in thin flakes. The salt is much less soluble in water than any of the other salts of this acid. It is insoluble in boiling strong alcohol.

0.1547 gram of salt lost, at 200°, 0.0206 gram H_2O and gave 0.0483 gram K_2SO_4 or 0.02165 gram K.

0.2582 gram salt lost, at 200°, 0.0339 gram H_2O and gave 0.0812 gram K_2SO_4 or 0.0364 gram K.

	Calculated for $C_6H_3\overset{CH_3}{\underset{OCH_3}{-}}SO_3K + 2H_2O.$	Found.	
		I.	II.
H_2O	13.05	13.33	13.13
K	14.13	14.00	14.09

Calcium Salt, $\left(C_6H_3\overset{CH_3}{\underset{OCH_3}{-}}SO_3\right)_2Ca + 4\frac{1}{2}C_2H_5OH.$—This salt crystallizes from alcohol, in which it is easily soluble, in color-

less, transparent crystals, which have the appearance of very much distorted octahedrons. After some time it was noticed that acicular crystals began to separate in the same solution. At this point the crystals first formed were removed for analysis.

Great difficulty was experienced in the analysis of this salt, owing to the fact that the last molecule of alcohol seems to be held more firmly than the others, and comes off only on long-continued heating at a high temperature. The heating in several cases was stopped before all the alcohol was driven off, as a slight change in color seemed to indicate that the salt was about to undergo decomposition. The results for calcium in all these cases were low when calculated on the basis of the alcohol-free salt, but when the calculation was made on the basis of the salt with alcohol of crystallization the results for calcium in three cases were constant.

0.2299 gram salt lost, at 210°, 0.0716 gram alcohol and gave 0.0485 gram $CaSO_4$, or 0.01426 gram Ca.

0.161 gram salt lost, at 210°, 0.0515 gram alcohol and gave 0.0332 gram $CaSO_4$, or 0.00976 gram Ca.

	Calculated for $\left(C_6H_3\begin{matrix}CH_3 \\ -SO_3 \\ OCH_3\end{matrix} \right)_2 Ca + 4\frac{1}{2}C_2H_5.OH.$	Found. I.	II.
$C_2H_5.OH$	31.41	31.15	31.99
Ca	6.07	6.20	6.06

The needles which separated last were again dissolved, after which crystals came down like the crystals first obtained and analyzed. There is reason for the belief that the two forms of crystals obtained were due to the differing concentration of the solution and that the needle-like crystals contained a different number of molecules of alcohol from those shaped somewhat like the distorted octahedron. (The latter crystals are not octahedrons, but simply present a striking resemblance to distorted octahedrons.) A salt of this nature, concerning which experimental data will be given, will be described later.

The salt which was crystallized from alcohol was powdered and heated for five hours in a drying-oven at 200°, in order

to remove the alcohol. It was then dissolved in water, and, on slow evaporation, transparent, colorless, long, monoclinic prisms separated. These crystals can remain in the air several days without any sign of efflorescing.

The utmost difficulty was experienced in obtaining anything like satisfactory results for the water contained in the salt. At a temperature of 210° the salt had a constant weight, but the calcium in every case was about 0.5 per cent low when calculated on the basis of the anhydrous salt. Long heating at 230° to 240° was found necessary in order to obtain the salt in an anhydrous condition. Extreme care had to be exercised, as the salt undergoes decomposition at almost the same temperature at which it loses its last trace of water.

0.2364 gram salt gave 0.0479 gram $CaSO_4$ or 0.01408 gram Ca.

0.2381 gram salt lost, at 235°, 0.0795 gram H_2O and gave 0.0482 gram $CaSO_4$, or 0.01417 gram Ca.

0.1904 gram salt lost, at 240°, 0.0622 gram H_2O and gave 0.0396 gram $CaSO_4$, or 0.01164 gram Ca.

	Calculated for $\left(C_6H_3 \begin{smallmatrix} CH_3 \\ -SO_3 \\ OCH_3 \end{smallmatrix} \right)_2 Ca + 12H_2O.$	Found.		
		I.	II.	III.
H_2O	32.83	....	33.39	32.66
Ca	6.08	5.96	5.95	6.11

Magnesium Salt, $\left(C_6H_3 \begin{smallmatrix} CH_3 \\ -SO_3 \\ OCH_3 \end{smallmatrix} \right)_2 Mg + 8H_2O.$—To a hot aqueous solution of the free sulphonic acid finely powdered magnesium oxide was added until the solution was exactly neutral. Light red, transparent, elongated prisms separated which, on second crystallization, were obtained in a colorless condition. The salt, on long exposure to air, lost part of its water of crystallization. The anhydrous salt, on exposure to air, again took up water, but the amount it absorbed was not determined.

0.2142 gram salt lost, at 150°, 0.0546 gram H_2O and gave 0.0146 gram MgO, or 0.00876 gram Mg.

0.202 gram salt lost, at 150°, 0.051 gram H_2O and gave 0.0137 gram MgO, or 0.0082 gram Mg.

	Calculated for $\left(C_6H_3{<}^{CH_3}_{SO_3}{\diagdown}_{OCH_3}\right)_2Mg + 8H_2O.$	Found. I.	II.
H_2O	25.26	25.24	25.49
Mg	4.21	4.09	4.07

Copper Salt, $\left(C_6H_3{\diagup}^{CH_3}_{\diagdown}{-}SO_3 \atop OCH_3\right)_2Cu + 6\frac{1}{2}H_2O.$—Two copper salts were made, the one by exactly precipitating the barium, in an aqueous solution of the barium salt, by means of a dilute solution of copper sulphate, and allowing the copper salt to crystallize slowly after filtering off the barium sulphate. The salt thus obtained had a slight blue color and was composed of needles.

Another salt was made by neutralizing the aqueous solution of the free sulphonic acid with freshly prepared copper oxide. The crystals of the salt thus prepared were needles having a slight green color. Probably neither of the salts was pure, but analyses showed both to be identical in composition. The results given under I. and II. are for the salt prepared by the second method; that under III. for the salt made by neutralizing the barium salt with copper sulphate.

0.2286 gram salt lost, at 150°, 0.0461 gram H_2O and gave 0.0312 gram CuO, or 0.0249 gram Cu.

0.1803 gram salt lost, at 150°, 0.0361 gram H_2O and gave 0.025 gram CuO, or 0.0199 gram Cu.

0.1582 gram salt lost, at 150°, 0.0321 gram H_2O and gave 0.021 gram CuO, or 0.01675 gram Cu.

	Calculated for $\left(C_6H_3{<}^{CH_3}_{SO_3}{\diagdown}_{OCH_3}\right)_2Cu + 6\frac{1}{2}H_2O.$ I.	II.	III.
H_2O	20.09	20.16	20.02	20.21
Cu	10.85	1 88	11.16	10.59

Zinc Salt, $\left(C_6H_3 \diagup^{CH_3}_{\diagdown OCH_3} -SO_3 \right)_2 Zn + 6\frac{1}{2}H_2O.$ —This salt was

prepared by neutralizing an aqueous solution of the free acid with zinc carbonate. After recrystallizing the yellow crystals which first separated, perfectly colorless prisms were obtained. The crystals effloresce on exposure to air.

0.208 gram salt lost, at 125°, 0.0421 gram H_2O and gave 0.0282 gram ZnO, or 0.2363 gram Zn.

0.2041 gram salt lost, at 125°, 0.0411 gram H_2O and gave 0.0278 gram ZnO, or 0.0223 gram Zn.

	Calculated for $\left(C_6H_3{\diagup^{CH_3}_{\diagdown OCH_3}}-SO_3 \right)_2 Zn + 6\frac{1}{2}H_2O.$	Found.	
		I.	II.
H_2O	20.03	20.24	20.13
Zn	11.13	11.36	10.93

Lead Salt, $\left(C_6H_3 \diagup^{CH_3}_{\diagdown OCH_3} -SO_3 \right)_2 Pb + 3H_2O.$ —The lead salt

was prepared by adding lead carbonate to a hot aqueous solution of the free acid. The crystals separating at first were composed of light-yellow, radiating fibers. These crystals were dissolved in strong alcohol in order to remove any lead carbonate or sulphate which might have crystallized with them. The alcoholic solution was then evaporated to dryness and the salt again crystallized from water, from which it was obtained in colorless needles that radiated from a central point.

0.2102 gram salt lost, at 115°, 0.0169 gram H_2O and gave 0.0964 gram $PbSO_4$, or 0.06579 gram Pb.

0.230 gram salt lost, at 115°, 0.0185 gram H_2O and gave 0.1057 gram $PbSO_4$, or 0.07214 gram Pb.

	Calculated for $\left(C_6H_3{\diagup^{CH_3}_{\diagdown OCH_3}}-SO_3 \right)_2 Pb + 3H_2O.$	Found.	
		I.	II.
H_2O	8.15	8.04	8.05
Pb	31.16	31.30	31.37

Fusion of Paramethoxymetatoluenesulphonic Acid with Potassium Hydroxide.

About 30 grams of potassium hydroxide were melted in a silver crucible and about 10 grams of the free acid, dissolved in water, were gradually added, after the temperature had fallen sufficiently to prevent spurting. The mass assumed a dark-red color, and after being heated for one-half hour at 180° to 200°, gradually turned white. A small portion of the mass was taken out, dissolved in water, and ᵔcidified with dilute hydrochloric acid. No odor of sulphur dioxide being perceptible, the fusion was continued, tests for sulphur dioxide being made at intervals of about five minutes. After heating for about an hour at the temperature above mentioned, a trace of sulphur dioxide was noticed, when a portion of the mass was dissolved in water and acidified with hydrochloric acid. The fusion was then discontinued and the entire mass dissolved in water and acidified with hydrochloric acid. Only a small amount of sulphur dioxide was given off. The solution was evaporated to dryness, the residue heated in a drying-oven at 130°, finely powdered, and extracted for ten minutes with boiling absolute alcohol. From the alcoholic filtrate, white needles separated. These needles were purified by dissolving them again in absolute alcohol, in which they are difficultly soluble. From concentrated aqueous solutions the substance separates in colorless, orthorhombic prisms. In this manner crystals 20 x 5 x 2 mm. were obtained. Analysis showed the substance to be a potassium salt. The salt crystallized from water melts at 244° and decomposes at 247°. The twin crystals form crosses and, in appearance, resemble the mineral staurolite.

0.2164 gram salt gave off, at 170°, 0.0297 gram H_2O and 0.0715 gram K_2SO_4, or 0.03204 gram K.

0.226 gram salt lost, at 190°, 0.0319 gram H_2O and gave 0.075 gram K_2SO_4, or 0.03361 gram K. The salt in this determination was slightly fused, which accounts for the high result for H_2O.

	Calculated for $C_6H_3{-}SO_2OK + 2H_2O.$ (with CH_3 above and OH below)	Found.	
		I.	II.
H_2O	13.74	13.77	14.11
K	14.88	14.83	14.81

Further Action of Potassium Hydroxide on Paramethoxymeta-toluenesulphonic Acid.

From the experiment above described it will be seen that the methoxy group is the least stable, and is most easily replaced by hydroxyl. The sulphonic acid group is very stable in this compound, and it requires a high temperature and fusion for about two hours to replace it by hydroxyl. The fused mass, after reaching the state in the experiment above described, must be stirred constantly to prevent charring. It finally turns deep-brown and becomes liquid, the change from the white, pasty mass to the semi-liquid condition being indicative of the complete replacement of the sulphonic acid group by hydroxyl. As soon as the mass assumed a liquid condition the heating was discontinued and the melt allowed to cool. It was then dissolved in water and acidified with hydrochloric acid and the solution extracted with ether. On evaporating the ether extract a small quantity of heavy, dark-colored oil was obtained. It was evidently impure, but the quantity was not sufficient to permit of its purification. The aqueous solution of this oil reduced an ammoniacal solution of silver nitrate and also Fehling's solution, and it gave a green color with ferric chloride. This agrees for the color reactions given for homopyrocatechol (methyl-1-dihydroxy-3,4-benzene), but the evidence is not regarded as conclusive that the substance is homopyrocatechol. Homopyrocatechol[1] is described as a brown syrup which, if distilled under diminished pressure, can be purified and made to solidify to a white mass, which melts at 49° to 50° and boils at 250° to 252°. It can be obtained in this condition only with great difficulty, and is generally obtained as a brown oil and recognized by its color reactions.

[1] Compt. rend., **115**, 234; **116**, 104; **118**, 809; **114**, 1543; Ber. d. chem. Ges., **10**, 210 J. Chem. Soc., **55**, 90; Ber. d. chem. Ges., **25**, 3533.

Paramethoxymetatoluenesulphone   Chloride. — The sodium
salt of paramethoxymetatoluenesulphonic acid was dried
at 120°, finely powdered, and placed in a porcelain dish.
To this salt an equal weight of phosphorus pentachlo-
ride was added and the mixture rubbed with a pestle.   In a
short time action took place and the mass turned to a light-
yellow, oily material which, on cooling, became solid.   It
was then washed with water and a portion dissolved in ben-
zene, from which it crystallized in light-yellow plates.   It is
soluble in ether and acetone.   From the latter solvent per-
fectly colorless, transparent plates can be obtained if the solu-
tion is evaporated slowly in a vacuum-desiccator.   These
plates melt at 83°.5 to 84°.   The same specimen, after it was
allowed to cool, again melted at the same point.

0.1852 gram substance gave 0.1199 gram AgCl, or 0.02966
gram Cl.

	Calculated for $C_6H_3{\overset{\text{CH}_3}{\underset{\text{OCH}_3}{-}}}SO_2Cl$.	Found.
Cl	16.06	16.02

Paramethoxymetatoluenesulphonamide. — The chloride ob-
tained as above described was finely powdered and 50
grams of it were placed in a beaker containing about 300
cc. strong ammonia and 200 cc. water.   No immediate
action was observed to take place, but on allowing the
mixture to stand over night the mass at the bottom of the
beaker changed from white to a dark-yellow color.   This
yellow mass was removed and crystallized from boiling water,
from which it separated in needles which melted at 180° to
181°.   It is insoluble in cold water, and soluble with great
difficulty in boiling water.   It is easily soluble in hot alcohol,
which is the best solvent for its purification.   From alcohol it
separates in white needles.   The ammoniacal solution was
evaporated to dryness, and on the addition of cold water
nearly the entire residue went into solution, showing that the
amide is practically insoluble in ammonia.

0.2073 gram substance gave 0.2415 gram $BaSO_4$.

0.219 gram substance gave 0.2516 gram $BaSO_4$.
0.2835 gram substance gave 0.0205464 gram N.

	Calculated for $C_6H_3{\scriptstyle\begin{array}{l}-CH_3\\-SO_2NH_2.\\-OCH_3\end{array}}$	I.	II.	III.
S	15.92	15.98	15.77	....
N	6.96	....	....	7.21

Preparation of Paramethoxymetasulphaminebenzoic Acid.

In a long-necked balloon flask, of 3 liters capacity, 180 grams of potassium permanganate were placed and 2 liters of water added. To this solution 50 grams of paramethoxy-metatoluenesulphonamide were added, the flask provided with a return-condenser, placed in a water-bath, and heated till the potassium permanganate was completely reduced. By this treatment it was expected that the methyl group would be oxidized to carboxyl.

When the purple color had entirely disappeared, the manganese hydroxide was filtered off and thoroughly washed with hot water. Strong hydrochloric acid was then added to the filtrate, and white needles separated. In order to remove any unoxidized amide, the material thus obtained was dissolved in dilute sodium carbonate in which the amide is insoluble. On addition of hydrochloric acid to the solution, the free acid again separated and was then crystallized from boiling water, in which it is sparingly soluble. Thus obtained, it melted at 252° to 277°, and repeated recrystallizations from water did not give a pure product. It was then dissolved in boiling absolute alcohol and obtained from this in a pure condition. Thus purified, it melted at 276° to 277°. At 274° there was a slight change in color, but no evidence of melting was observed on keeping the temperature at that point for some time. From alcohol both needles and plates were obtained from the same solution, but the melting-point of each indicated that they were identical except in crystal form. As a result of several experiments, it is believed that when the temperature of the water-bath, in which the flask is placed during the oxidation process, is not raised above 85° the yield

of the oxidation-product is greater than when the water in the bath is allowed to boil constantly. Almost a quantitative yield was obtained by slow oxidation at 85°, whereas, when the temperature was raised to about 100°, the quantity obtained was less than half of the theoretical.

0.2968 gram acid gave 0.0186 gram N.

0.3055 gram acid gave 0.019177 gram N.

0.2521 gram acid gave 0.2554 gram $BaSO_4$.

0.2802 gram acid gave 0.2838 gram $BaSO_4$.

0.2026 gram acid gave 0.3062 gram CO_2 and 0.0733 gram H_2O.

	Calculated for $C_6H_3{-}{\begin{smallmatrix}COOH\\SO_2NH_2\\OCH_3\end{smallmatrix}}$	Found.				
		I.	II.	III.	IV.	V.
C	41.56	41.21	....	....	....	....
H	3.89	4.02	....	....	....	....
N	6.06	....	6.27	6.28	....	....
S	13.85	....	....	....	13.91	13.97

Sodium Salt, $C_6H_3{-}{\begin{smallmatrix}COONa\\SO_2NH_2\\OCH_3\end{smallmatrix}} + 3H_2O$.—This salt separates from water in needles which have a slight cream color, but are transparent. The salt is insoluble in strong hot alcohol.

0.2364 gram salt lost, at 160°, 0.0372 gram H_2O and gave 0.0557 gram Na_2SO_4, or 0.01803 gram Na.

0.2623 gram salt lost, at 160°, 0.0414 gram H_2O and gave 0.062 gram Na_2SO_4, or 0.02008 gram Na.

	Calculated for $C_6H_3{-}{\begin{smallmatrix}COONa\\SO_2NH_2\\OCH_3\end{smallmatrix}} + 3H_2O$.	Found.	
		I.	II.
H_2O	15.95	15.74	15.79
Na	7.64	7.62	7.65

Potassium Salt, $C_6H_3{-}{\begin{smallmatrix}COOK\\SO_2NH_2\\OCH_3\end{smallmatrix}} + 1\frac{1}{2}H_2O$.—The potassium salt crystallizes from water in extremely fine, almost colorless,

needles. It is very soluble in water and good crystals are obtained with difficulty. It is insoluble in cold alcohol.

0.3046 gram salt lost, at 210°, 0.0276 gram H_2O and gave 0.0889 gram K_2SO_4, or 0.03985 gram K.

0.2886 gram salt lost, at 210°, 0.0263 gram H_2O and gave 0.0842 gram K_2SO_4, or 0.0377 gram K.

	Calculated for $C_6H_3\diagdown \begin{matrix}COOK\\-SO_2NH_2\\OCH_3\end{matrix} + 1\frac{1}{2}H_2O.$	Found.	
		I.	II.
H_2O	9.12	9.06	9.11
K	13.18	13.08	13.08

Calcium Salt, $\left(C_6H_3\diagup\begin{matrix}COO\\-SO_2NH_2\\OCH_3\end{matrix} \right)_2Ca + 5H_2O.$—This forms white, glistening needles, arranged in clusters. It can be exposed to the air without losing its water. It is insoluble in cold or hot strong alcohol.

0.2195 gram salt lost, at 235°, 0.0335 gram H_2O and gave 0.0497 gram $CaSO_4$, or 0.01461 gram Ca.

0.2245 gram salt lost, at 235°, 0.0341 gram H_2O and gave 0.0503 gram $CaSO_4$, or 0.01479 gram Ca.

	Calculated for $\left(C_6H_3\diagup\begin{matrix}COO\\-SO_2NH_2\\OCH_3\end{matrix}\right)_2Ca + 5H_2O.$	Found.	
		I.	II.
H_2O	15.25	15.27	15.19
Ca	6.77	6.65	6.59

Barium Salt, $\left(C_6H_3\diagup\begin{matrix}COO\\-SO_2NH_2\\OCH_3\end{matrix} \right)_2Ba + 4\frac{1}{2}H_2O.$—This appears in the form of colorless needles, radiating from a center and in form resembling a chestnut burr. It is almost insoluble in alcohol, but easily soluble in cold water. In order to dehydrate the salt completely it was necessary to heat it for a long time at 245°. It decomposes at about 255°.

0.3400 gram salt lost, at 245°, 0.041 gram H_2O and gave 0.1174 gram $BaSO_4$, or 0.069 gram Ba.

0.3314 gram salt lost, at 245°, 0.0396 gram H_2O and gave 0.1154 gram $BaSO_4$, or 0.0679 gram Ba.

	Calculated for $\left(C_6H_3\genfrac{}{}{0pt}{}{\genfrac{}{}{0pt}{}{COO}{SO_2NH_2}}{OCH_3} \right)_2 Ba + 4\frac{1}{2}H_2O.$	Found. I.	II.
H_2O	11.93	12.06	11.95
Ba	20.29	20.33	20.49

Magnesium Salt, $\left(C_6H_3\genfrac{}{}{0pt}{}{\genfrac{}{}{0pt}{}{COO}{SO_2NH_2}}{OCH_3} \right)_2 Mg + 6H_2O.$ —— This

separates from water in fine, silky needles. These needles, when removed from the solution for the purpose of drying, were accidentally placed in a warm place and they went into solution. From this concentrated solution colorless crystals, which have the appearance of thick, triclinic prisms, separated. These crystals were remarkable for their iridescence. It was noticed that from the same solution both needles and prisms would separate, only a few prisms crystallizing when the solution was dilute and the needles compact. Analysis of the prismatic crystals gave the following result :

0.2901 gram salt lost, at 225°, 0.0521 gram H_2O and gave 0.0201 gram MgO, or 0.01207 gram Mg.

0.2328 gram salt lost, at 235°, 0.0428 gram H_2O.

0.2533 gram salt gave 0.0172 gram MgO, or 0.01033 gram Mg.

It was found necessary to add fine ammonium carbonate in order to get rid of the sulphonic acid residue. Without this addition the results for magnesium were high, showing that magnesium sulphate had probably been formed.

	Calculated for $\left(C_6H_3\genfrac{}{}{0pt}{}{\genfrac{}{}{0pt}{}{COO}{SO_2NH_2}}{OCH_3} \right)_2 Mg + 6H_2O.$	Found. I.	II.
H_2O	18.24	17.96	18.34
Mg	4.05	4.16	4.08

Analysis of the air-dried acicular crystals indicated that they contained 10.5 molecules of water. Both kinds of crystals were exposed to the air without losing their water of crystallization.

Fusion of Paramethoxymetasulphaminebenzoic Acid with Potassium Hydroxide.

About 40 grams of potassium hydroxide were heated with a little water in a silver dish until the alkali was dissolved. About 5 grams of the paramethoxymetasulphaminebenzoic acid were then added. The addition of the acid is most conveniently made by first dissolving it in aqueous potassium hydroxide and then adding the solution slowly. The fusion was carried on for about twenty minutes, care being taken to avoid too high a temperature in order that the compound might not be entirely broken down. The mass was then dissolved in water and acidified with hydrochloric acid. No odor of sulphur dioxide was perceptible, showing that the group SO_2NH_2 had not been replaced by hydroxyl. On standing for some time in a cool place, white needles separated. The crystals were arranged in radiating clusters and had a more blunt, prism-like appearance than the corresponding methoxy compound. The compound crystallizes well from alcohol, and is more soluble in water than the paramethoxymetasulphaminebenzoic acid. Its melting-point is 258°, and it decomposes at about 265°. Analysis shows it to be parahydroxymetasulphaminebenzoic acid.

0.3049 gram acid gave 0.01999 gram N.

0.3065 gram acid gave 0.02033 gram N.

0.2022 gram acid gave 0.0528 gram H_2O, or 0.00587 gram H, and 0.285 gram CO_2, or 0.0777 gram C.

0.2413 gram acid gave 0.2605 gram $BaSO_4$, or 0.0358 gram S.

	Calculated for $C_6H_3\begin{cases}COOH\\SO_2NH_2\\OH\end{cases}$	Found.			
		I.	II.	III.	IV.
C	38.76	....	....	....	38.44
H	3.22	....	....	....	2.90
N	6.45	6.56	6.63	....	....
S	14.75	....	....	14.83	....

Sodium Salt, $C_6H_3\begin{cases}COONa\\SO_2NH_2\\OH\end{cases} + 4H_2O.$ — This salt forms

white, radiating needles which are very soluble in water but insoluble in boiling, strong alcohol.

0.2203 gram salt lost, at 170°, 0.0506 gram H_2O and gave 0.0499 gram Na_2SO_4, or 0.01616 gram Na.

	Calculated for $C_6H_3{<}^{COONa}_{SO_2NH_2}{\cdot}{OH} + 4H_2O.$	Found.
H_2O	23.15	22.97
Na	7.40	7.34

Barium Salt, $\left(C_6H_3{<}^{COO}_{SO_2NH_2}{\cdot}{OH} \right)_2Ba + 6\frac{1}{2}H_2O.$ —This separated in white tufts, which are easily soluble in water and insoluble in boiling alcohol.

0.2381 gram salt lost, at 240°, 0.0403 gram H_2O and gave 0.0812 gram $BaSO_4$, or 0.0478 gram Ba.

	Calculated for $\left(C_6H_3{<}^{COO}_{SO_2NH_2}{\cdot}{OH} \right)_2Ba + 6\frac{1}{4}H_2O.$	Found.
H_2O	17.03	16.93
Ba	20.01	20.06

Further Action of Potassium Hydroxide on Paramethoxymeta-sulphaminebenzoic Acid.

It was found in a previous experiment that the methoxy group in the methoxysulphamine acid could be replaced by hydroxyl without the removal of the sulphamine group. In order to test the further action of potassium hydroxide on this acid, 20 grams of potassium hydroxide were placed, together with a little water, in a silver dish and melted. To this mass about 3 grams of the methoxysulphamine acid were gradually added, and the mass fused, at a high temperature, for about two hours. On dissolving the mass, and acidifying it with hydrochloric acid, sulphur dioxide was given off in abundance. The acidified solution was then extracted with ether, the ether evaporated, and a dark, semi-crystalline mass obtained. This was dissolved in alcohol, from which it separa.

ted in yellow crystals, which melted at 187° to 192°. This material reduced an ammoniacal solution of silver nitrate, but had no effect on Fehling's solution. Ferric chloride added to an aqueous solution of the substance produced a blue-green color, which turned red on the addition of sodium carbonate. This is clear evidence that the substance is protocatechuic acid, and is, therefore, confirmatory evidence that the sulphamine group is in the meta position.

Discussion of the Evidence which Shows that the Sulphonic Acid Group in Paramethoxymetatoluenesulphonic Acid is in the Meta Position.

There are two possibilities for the entrance of a single SO_2OH group, in paramethoxytoluene, which may be represented by formulas I. and II.:
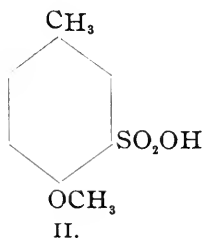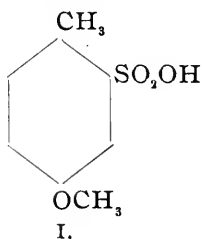
The first, by the replacement of the methoxy and sulphamine groups by hydroxyl, by fusion with potassium hydroxide, should yield methyl-1-dihydroxy-2,4-benzene ; the second, by similar treatment, should give homopyrocatechol or methyl-1-dihydroxy-3,4-benzene. It is believed that the latter product was obtained, but the evidence on this point is not conclusive.

By treatment with phosphorus pentachloride, the sodium salt of the sulphonic acid (I.) should yield a chloride,

$C_6H_3\begin{smallmatrix}CH_3\\ \\OCH_3(p)\end{smallmatrix}SO_2Cl(o)$, and this, on treatment with ammonia, should
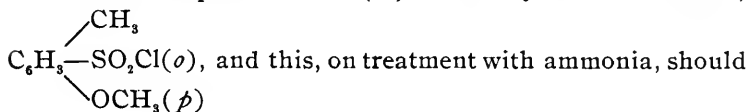
give the amide, $C_6H_3\begin{smallmatrix}CH_3\\ \\OCH_3(p)\end{smallmatrix}SO_2NH_2(o)$. On oxidizing this amide

with potassium permanganate a sulphinide would be obtained

having the formula C_6H_5—$SO_2$$\diagup^{CO}_{\diagdown OCH_3}{>}NH$. All these compounds

were made by Parks,[1] working in this laboratory. The compounds which Parks obtained agree in no respect with those obtained by the writer. The chloride made by Parks is an oil ; the amide is composed of white needles and melts at 150°, and the sulphinide, of needles which melt at 271°.

Metcalf,[2] working in this laboratory, by diazotizing paratoluidinemetasulphonic acid, decomposing the product with methyl alcohol, and then treating the sodium salt of the resulting compound with phosphorus pentachloride, obtained a

chloride which had the formula $C_6H_3\diagup^{CH_3}_{\diagdown OCH_3(p)}{-}SO_2Cl(m)$. From this

chloride he obtained the amide $C_6H_3\diagup^{CH_3}_{\diagdown OCH_3(p)}{-}SO_2NH_2(m)$, and on

oxidizing this a compound, which he took to be

$C_6H_3\diagup^{COOH}_{\diagdown OCH_3(p)}{-}SO_2NH_2(m)$, although it was impure, as indicated by

its melting-point.

The compounds the writer obtained agree with those which Metcalf made. In addition to this the writer, by fusing the

acid, $C_6H_3\diagup^{COOH}_{\diagdown OCH_3(p)}{-}SO_2NH_2(m)$, with potassium hydroxide obtained

protocatechuic acid, $C_6H_3\diagup^{COOH}_{\diagdown OH(p)}{-}OH(m)$. All these facts go to

show that the group SO_2OH entered in the meta position, and

[1] This JOURNAL, 15, 320.
[2] *Ibid.*, 15, 301.

that the sulphonic acid first formed is that indicated by formula II, or paramethoxymetatoluenesulphonic acid.

Summary of Results.

1. When paradiazotoluene sulphate is decomposed, at the ordinary pressure, with methyl alcohol in the presence of the compounds formed during the diazotizing process, both the methoxy and hydrogen reactions take place ; the latter, however, to a very small extent.

2. When paramethoxytoluene is treated with sulphuric acid but one sulphuric acid residue enters the compound, and the sulphonic acid group takes the meta position.

3. When paramethoxymetatoluenesulphonic acid is fused with potassium hydroxide at a comparatively low temperature, potassium parahydroxymetatoluenesulphonate is formed ; at higher temperatures homopyrocatechol appears to be formed.

4. When oxidized with potassium permanganate, paramethoxymetatoluenesulphonamide yields paramethoxymetasulphaminebenzoic acid.

5. When paramethoxymetasulphaminebenzoic acid is cautiously fused with potassium hydroxide parahydroxymetasulphaminebenzoic acid is obtained ; on prolonged fusion at a high temperature, protocatechuic acid is formed.

VI.—CHEMICAL CHANGES IN CHEESE-RIPENING AS AFFECTED BY DIFFERENT CONDITIONS.

By Lucius L. Van Slyke and Edwin B. Hart.

The object of this article is to present the results of our study relating to some of the more prominent conditions that influence the chemical changes taking place in the nitrogen compounds of cheese during the ripening process. It is well known that, during the cheese-making process, chemical changes soon begin in the freshly coagulated curd or paracasein formed when milk casein is acted upon by rennet. The same cheese examined at intervals is found to show quite

marked variations in the character of its nitrogen compounds. Cheeses made from the same milk under the same conditions of manufacture and subjected to different conditions during the ripening process show a difference in chemical composition. Cheeses manufactured under different conditions and ripened under uniform conditions may vary in the character of their nitrogen compounds. It has seemed to us desirable that a somewhat comprehensive study should be made of the changes actually found in the nitrogen compounds of cheese, using in the work only cheeses made and ripened under known, controlled conditions. The results presented in this article by no means exhaust the subject, our intention being to study first only some of the more prominent factors, such as time, temperature, moisture, salt, rennet, and acid.

The chief proteid of curd, freshly coagulated by rennet, consists, under usual conditions, of a compound called paracasein, in some respects resembling milk-casein, in other respects differing from it in a marked degree. The exact chemical relation of these two compounds has not yet been learned. In the usual methods of cheese-making the milk sugar, acted on by certain organisms, begins to form lactic acid early in the process, and this acid, as rapidly as formed, combines chemically with paracasein to form a compound called paracasein monolactate. Many of the peculiar properties of curd are believed to be due to the presence of this paracasein monolactate, such as the ability to form fine strings on a hot iron, the changes in appearance, plasticity and texture, and, perhaps, the shrinking. It is also probable that paracasein monolactate forms the real starting-point of cheese ripening, or, stated another way, that we must have paracasein monolactate present before we can have formed such compounds as caseoses, peptones, and amides. Starting with the casein of milk, we have in cheese-curd and ripening cheese the following nitrogen compounds formed in something like the following order : Paracasein, paracasein monolactate, paranuclein, caseoses, peptones, amido compounds, and ammonia compounds. The amounts of these different compounds and classes of compounds, and their relations to one another, we shall study in some detail in the following pages.

The Relation of Time to the Chemical Changes of Cheese-Ripening.

As we shall point out later, the effect of time as a factor in cheese-ripening is modified by a variety of conditions. For purpose of illustration, we will here give averages of the results obtained under various conditions. Each analysis represents averages of the results obtained with 24 different cheeses.

Table I.—Showing Effect of Time on Cheese-ripening.

Nitrogen, expressed as percentage of nitrogen in cheese, in form of

Age of cheese.	Paracasein monolactate.	Water-soluble nitrogen comp'ds.	Paranuclein.	Caseoses.	Peptones.	Amides.	Ammonia.
Months.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per c't.
$1\frac{1}{2}$	20.18	21.44	2.06	3.15	3.84	9.88	1.56
3	27.26	30.98	4.45	4.56	4.65	14.36	2.45
6	27.55	36.15	3.57	4.92	4.22	19.96	3.52
9	24.14	43.45	4.02	4.59	3.56	26.53	4.74
12	19.04	44.75	3.52	4.16	3.95	28.38	5.41
18	12.65	47.25	3.40	3.88	2.57	30.46	6.62

The data embodied in this table suggest the following statements:

(1) The total amount of nitrogen in the form of water-soluble compounds increases as the cheese gains in age. This increase is more rapid in the early stages of ripening. Of the total amount of water-soluble nitrogen compounds formed in the cheese during eighteen months, 45.4 per cent was formed in the first month and a half; 65.5 per cent in the first three months; 76.5 per cent in the first six months; and 92 per cent in the first nine months, or one-half the entire period covered by the study.

(2) The nitrogen in the form of paracasein monolactate appears to increase for six months and then gradually decrease. However, these data are not calculated to show the variations of this compound to advantage, since we have learned from other work of ours that paracasein monolactate commonly ap-

pears at its maximum quantity in fresh cheese and is very largely changed into other forms in the course of a few weeks, the rapidity of its appearance and disappearance being dependent upon such conditions as the acidity of the cheese, the temperature of the curing room, etc.

(3) The nitrogen in the form of paranuclein, caseoses, and peptones varies comparatively little, but there is a general tendency to a decrease in amount with increase of age in cheese.

(4) The amido compounds increase with comparative rapidity during the early stages of ripening. The increase continued during the whole period of study but at a less rapid rate. Thus, of the entire amount of amido compounds formed during eighteen months, 87 per cent was found at the end of nine months, and about 33 per cent at the end of one month and a half.

(5) The ammonia in cheese does not commonly reach an appreciable quantity until cheese is about a month old, after which it increases quite regularly. It forms less slowly in the later than in the early stages of ripening. Considerably over half the ammonia was formed in the first six months.

The Relation of Temperature to the Chemical Changes of Cheese-ripening.

In general, we find in every individual cheese that temperature exerts a marked influence upon the changes taking place in the nitrogen compounds. The effect of temperature is modified by other conditions. In the table on the following page we consider, along with the temperature, the time factor.

Summarizing our results, we find that, other conditions being uniform, (*a*) the water-soluble nitrogen compounds in cheese increase on an average very closely in proportion to increase of temperature ; (*b*) from the average of our results, there is an increase of 0.5 per cent of water-soluble nitrogen compounds for an increase of 1° of temperature between the limits of 32° F. and 70° F. ; (*c*) the amido compounds and ammonia are formed in the cheese more abundantly at higher

Table II.—Showing Effect of Temperature on Cheese-ripening.

Temperature of curing-room. Degrees F.	Form of nitrogen compound.	Nitrogen, expressed as percentage of nitrogen, in cheese.					
		One and a half months. Per cent.	Three months. Per cent.	Six months. Per cent.	Nine months. Per cent.	Twelve months. Per cent.	Eighteen months. Per cent.
32	Total water-soluble	12.80	18.64	23.06	32.66	34.02	36.75
55	"	20.56	31.46	36.09	43.91	45.09	49.40
60	"	23.14	33.69	39.97	46.89	48.62	50.16
70	"	29.24	40.13	45.50	50.34	51.25	52.67
32	Paracasein monolactate	20.58	43.14	36.55	43.00	34.48	21.37
55	"	33.01	33.66	35.10	25.61	19.26	19.45
60	"	13.89	18.81	19.94	16.15	12.32	9.45
70	"	13.24	13.45	18.62	11.83	10.10	7.86
32	Paranuclein	1.27	4.05	3.44	4.47	4.15	4.12
55	"	2.39	5.34	4.25	4.27	3.64	3.68
60	"	2.54	4.71	3.90	4.23	3.59	4.73
70	"	2.03	3.71	2.68	3.13	2.45	2.60
32	Caseoses	1.05	2.97	5.24	4.29	4.17	5.06
55	"	4.08	4.50	5.03	4.76	4.73	4.27
60	"	3.44	6.14	6.03	5.07	3.68	3.00
70	"	4.07	4.63	3.37	4.24	4.12	3.20
32	Peptones	1.30	2.23	4.53	4.36	4.53	4.17
55	"	3.90	4.95	3.99	3.10	3.72	2.84
60	"	3.33	5.99	4.70	3.44	4.03	1.80
70	"	4.07	5.45	3.67	3.33	3.51	1.50
32	Amides	4.82	6.36	8.70	17.55	18.73	19.44
55	"	8.69	14.33	19.55	27.05	29.00	31.66
60	"	12.16	14.55	21.39	28.84	31.14	33.54
70	"	13.86	22.20	30.80	32.68	34.65	37.19
32	Ammonia	0.61	0.61	1.21	1.91	2.14	3.98
55	"	1.50	2.42	3.30	4.69	5.57	6.95
60	"	1.67	2.54	3.89	5.43	6.12	7.35
70	"	2.47	4.22	5.71	6.91	7.49	8.19

temperatures and accumulate in the cheese, while the other water-soluble compounds of nitrogen and also paracasein monolactate do not appear to be regularly influenced by temperature in the early stages of ripening, but after some months they decrease in quantity with increase of temperature.

The Relation of Moisture to the Chemical Changes of Cheese-ripening.

In order to study the effect of moisture in cheese upon the chemical changes taking place in the nitrogen compounds, two sets of cheeses were made for comparison, four different cheeses in each set being made under parallel conditions. The cheeses designated as 42 were covered with melted paraffin, in order to retard the evaporation of water from the cheese. Those designated as 39 were left in the usual condition. These cheeses were all kept in the same curing-room at a temperature of 55° F. (See Table III.)

Comparing the results presented in Table III. we notice the following points of difference :

(1) The cheeses covered with paraffin had somewhat less water when made but the others lost water more rapidly, so that at the end of three months their water-content was about the same. After this the paraffined cheese contained considerably more water, the difference increasing with age, until at the end of 12 months it was over 4.5 pounds per 100 pounds of cheese.

(2) During the first three months the amount of water-soluble nitrogen compounds was about the same in both kinds of cheese, but from this point the amount increased more rapidly in the cheeses covered with paraffin, that is, in those cheeses containing more moisture. The difference becomes more marked at each succeeding analysis.

(3) After six months the paracasein monolactate disappears much more rapidly in the cheeses containing more moisture, the difference increasing up to twelve months.

The Relation of Salt in Cheese to the Chemical Changes of Cheese-ripening.

In Bulletin No. 203 of this Station, page 241, attention is

Table III.—Showing Effect of Moisture in Cheese on Cheese-ripening.

No. of cheese.	Form of nitrogen compound.	Nitrogen expressed as percentage of nitrogen in cheese.					
		One and a half months. Per cent.	Three months. Per cent.	Six months. Per cent.	Nine months. Per cent.	Twelve months. Per cent.	Eighteen months. Per cent.
39	Total water-soluble	17.32	27.09	31.76	39.09	39.80	42.77
42	" "	17.14	27.40	36.41	46.59	54.52	56.76
39	Paracasein monolactate	24.89	41.59	35.43	28.81	21.70	13.72
42	" "	21.17	30.42	49.29	20.16	9.81	5.30
39	Paranuclein	2.70	5.32	4.77	4.20	3.79	4.10
42	"	0.87	4.35	4.45	4.89	8.01	7.90
39	Caseoses	2.99	5.80	4.24	4.41	4.19	4.26
42	"	3.58	3.64	5.38	5.06	4.32	4.70
39	Peptones	2.12	4.09	3.75	3.57	3.97	1.95
42	"	4.49	4.80	6.19	4.00	4.43	3.20
39	Amides	7.50	9.79	16.00	21.65	22.89	26.73
42	"	7.22	12.59	17.12	26.03	29.44	29.00
39	Ammonia	1.34	2.15	3.04	4.17	4.53	5.72
42	"	0.98	1.99	4.26	6.52	8.27	12.16
39	Water	36.40	35.27	32.41	27.86	28.02	27.75
42	"	35.96	35.00	33.37	33.24	32.66	32.10

Table IV.—Showing Effect of Salt on Cheese-ripening.

Amount of salt used for 1000 lbs. of milk. Lbs.	Form of nitrogen compound.	Nitrogen expressed as percentage of nitrogen in cheese.					
		One and a half months. Per cent.	Three months. Per cent.	Six months. Per cent.	Nine months. Per cent.	Twelve months. Per cent.	Eighteen months. Per cent.
0	Total water-soluble	23.42	34.26	40.52	49.10	51.38	53.96
1.5	"	21.80	32.10	37.67	44.13	45.88	50.73
2.5	"	21.67	29.92	34.73	42.93	43.52	44.65
5	"	18.84	27.70	31.70	37.64	38.19	39.62
0	Paracasein monolactate	17.33	27.06	23.27	21.82	16.75	12.56
1.5	"	20.86	28.43	26.16	22.38	17.98	12.61
2.5	"	21.81	24.47	28.30	23.54	18.04	13.74
5	"	20.73	29.02	32.49	28.81	23.41	11.71
0	Paranuclein	1.85	4.44	3.80	4.66	3.83	3.44
1.5	"	2.13	4.47	3.52	4.01	3.72	3.89
2.5	"	2.27	4.55	3.51	3.80	3.30	3.34
5	"	1.98	4.35	3.42	3.63	3.23	2.96
0	Caseoses	3.41	4.94	4.94	5.60	4.95	3.87
1.5	"	3.24	5.02	5.17	4.53	3.69	4.04
2.5	"	3.21	4.14	4.98	4.16	3.97	3.84
5	"	2.75	4.14	4.58	4.08	4.05	3.77
0	Peptones	4.86	5.02	4.84	3.47	4.13	2.69
1.5	"	3.50	5.16	4.29	3.54	4.87	3.40
2.5	"	4.20	4.02	4.02	3.97	3.98	2.07
5	"	2.91	4.42	3.74	3.25	2.81	2.14

Table IV.—Showing Effect of Salt on Cheese-ripening (Continued).

Amount of salt used for 1000 lbs. of milk. Lbs.	Form of nitrogen compounds.	Nitrogen expressed as percentage of nitrogen in cheese.					
		One and a half months. Per cent.	Three months. Per cent.	Six months. Per cent.	Nine months. Per cent.	Twelve months. Per cent.	Eighteen months. Per cent.
0	Amides	10.22	15.86	22.18	28.89	32.19	35.09
1.5	"	10.46	14.77	20.13	27.31	29.33	32.36
2.5	"	9.78	13.83	19;20	26.72	27.61	29.57
5	"	8.82	12.97	17.34	23.21	24.40	24.81
0	Ammonia	1.67	2.96	4.64	6.54	7.77	8.89
1.5	"	1.67	2.53	3.69	4.69	5.36	7.04
2.5	"	1.51	2.36	3.13	4.30	4.54	5.83
5	"	1.41	2.03	2.64	3.43	3.61	4.70
0	Per cent water in cheese	39.27	38.22	35.60	35.22	34.09	30.96
1.5	" " " "	36.66	35.60	33.50	32.62	31.61	28.80
2.5	" " " "	35.69	34.43	32.31	31.54	30.99	27.68
5	" " " "	33.63	32.62	29.52	29.88	28.61	26.97
0	Per cent salt in cheese	0	0	0	0	0	0
1.5	" " " "	0.59	0.70	0.84	0.94	0.92	....
2.5	" " " "	0.82	1.20	1.15	1.26	1.27	....
5	" " " "	1.29	1.50	1.62	1.87	1.83	....

called to the fact that salt exerts a retarding influence upon the proteolytic action of enzymes in cheese. Since the results given there were secured with cheese made and kept in the presence of chloroform, it was desired to make a study of the influence of salt upon the ripening process in cheese normally made and kept under normal conditions. For the purpose of such a study, 4 different lots of cheese were made under normal conditions as nearly alike as possible, and salt was added to these in proportions varying as follows: No salt, 1.5, 2.5, and 5 pounds of salt for 1,000 pounds of milk. In Table IV. we give the averages of the different lots of cheeses.

We are to regard the salt in cheese as being in solution in the whey held by the cheese, practically forming a dilute brine. In common practice, cheesemakers add from 2 to 2.5 pounds of salt to the curd made from 1,000 pounds of milk. Cheese thus salted contains about 1 per cent of salt. Such cheese usually contains about 35 to 37 per cent of water. Consequently, under such conditions we should have approximately a 3 per cent brine. It is evident that in proportion as a cheese loses moisture by evaporation, the salt brine remaining becomes more concentrated with the advancing age of the cheese.

A study of the data contained in Table IV. enables us to make the following statements:

(1) The amount of salt retained in cheese is not proportional to the amount of salt added to the curd. Of necessity, a considerable proportion of the salt added to cheese curd passes into the whey.

(2) An increase of salt in cheese curd results in decreasing the amount of moisture held in cheese.

(3) An increase of salt in cheese was accompanied by a decrease in the amount of water-soluble nitrogen compounds and this was true through the whole eighteen months of the investigation. While this influence of salt is more noticeable in the case of the amido compounds and ammonia, it is clearly evident in the case of the paranuclein, caseoses, and peptones.

(4) The paracasein monolactate disappears less rapidly in the cheeses containing more salt.

It is readily seen from the results embodied in Table IV. that the rapidity of formation of water-soluble nitrogen compounds is decreased in the presence of increased amounts of salt in cheese. The question arises whether this is due directly to a retarding action of salt upon the agencies that cause cheese-ripening or to the effect of salt in decreasing the amount of moisture held in cheese. It is true that some of the observed differences in proteolysis can be accounted for by the difference in moisture-content noticed in the various cheeses. While this set of experiments does not clearly demonstrate that salt has in itself a direct retarding effect upon the cheese-ripening process, we have some results obtained with another experiment which indicate that salt has a retarding effect upon proteolysis in cheese. In some experiments made in another line of work, salt clearly exerted a retarding influence upon the formation of water-soluble nitrogen compounds. Then, again, some work carried on with milk, where there was no difference of water-content, indicates the same retarding action of salt.

The Relation of Varying Amounts of Rennet-Enzyme to the Chemical Changes of Cheese-ripening.

In Bulletin No. 54, page 267, are given the results of some experiments made in 1892 at this Station, when a comparison was made of the amount of water-soluble nitrogen formed in cheeses made with 3 and 9 ounces of rennet-extract per 1000 pounds of milk. Considerably larger amounts of soluble nitrogen were found when the larger amount of rennet was used. In 1899 some further experiments were made, using 3 and 6 ounces of Hansen's rennet-extract for 1000 pounds of milk. The cheeses were so made as to contain about the same amount of moisture.

The data embodied in Table V. show quite generally a greater increase of water-soluble nitrogen compounds in the cheese containing the larger amount of rennet.

If we examine the different classes of the water-soluble nitrogen compounds, we notice that the increase caused by increased use of rennet is more noticeable in the case of the

Table V.—Showing Effect of Different Amounts of Rennet upon Cheese-ripening.

Age of cheese.	Amount of rennet-extract used for 1,000 pounds of milk.	Perc'tage of water in cheese.	Nitrogen expressed as percentage of nitrogen in cheese in form of			
			Water-soluble nitrogen.	Paranuclein, caseoses, and peptones.	Amides.	Ammonia.
Months.	Ounces.		Per cent.	Per cent.	Per cent.	Per cent.
I	3	37.54	18.90	10.31	8.36	....
I	6	38.06	23.40	13.37	9.47	....
3	3	35.59	26.70	13.34	12.00	1.87
3	6	36.25	29.70	15.40	12.50	1.86
6	3	33.58	29.80	12.02	16.20	2.09
6	6	33.51	35.40	15.11	18.20	2.60
9	3	31.84	37.30	13.47	21.20	2.59
9	6	30.63	35.50	13.00	20.00	2.50
12	3	28.13	38.00	12.05	22.10	4.10
12	6	29.98	42.40	14.38	24.00	3.60
15	3	26.73	39.10	12.05	22.90	4.53
15	6	25.97	43.60	13.19	25.50	4.31
24	3	24.76	42.70	12.30	25.10	5.06
24	6	23.33	48.50	14.54	28.50	5.84

paranuclein, caseoses, and peptones than in the case of the amides and ammonia, especially during the first six or nine months. After a year, the tendency is for a greater difference among the amides caused by increased use of rennet than between the other soluble nitrogen compounds.

These results are in harmony with some work done by Babcock, Russell, and Vivian,[1] who used 3, 9, 12, 18, and 24 ounces of rennet-extract per 1,000 pounds of milk, and made analyses of the cheese at one, two, and six months. In this period of time they found that, while there was a constant increase in the amount of total water-soluble nitrogen compounds when there was an increase in the amount of rennet used, this increase came mostly to the caseoses and peptones, the amides and ammonia remaining quite constant.

[1] Ann. Rep., Wis. Expt. Sta., **17**, 102 (1900).

Summary and Discussion of Results.

Reviewing briefly the results that have been presented in the preceding pages, we have found that different conditions affect the chemical changes in the nitrogen compounds of cheese as follows :

(1) *Time.*—The formation of water-soluble nitrogen compounds increases as cheese ages, other conditions being uniform. The rate of increase is, however, not uniform, since it is much more rapid in the early, than in the succeeding, stages of ripening.

(2) *Temperature.*—The amount of soluble nitrogen compounds increases, on an average, quite closely in proportion to increase of temperature, when other conditions are uniform.

(3) *Moisture.*—Other conditions being alike, there is formed a larger amount of water-soluble nitrogen compounds in cheese containing more moisture than in cheese containing less moisture.

(4) *Size.*—Cheeses of large size usually form water-soluble compounds more rapidly than smaller cheeses under the same conditions, because large cheeses lose their moisture less rapidly and after the early period of ripening have a higher water-content.

(5) *Salt.*—Cheese containing more salt forms water-soluble nitrogen compounds more slowly than cheese containing less salt. This appears to be due, in part, to the direct action of salt in retarding the activity of one or more of the ripening agents and, in part, to the tendency of the salt to reduce the moisture.content of the cheese.

(6) *Rennet.*—The use of increased amounts of rennet-extract in cheese-making, other conditions being uniform, results in producing increased quantities of water-soluble nitrogen compounds in a given period of time, especially such compounds as paranuclein, caseoses, and peptones.

(7) *Acid* appears to be essential to the formation of water-soluble nitrogen compounds in normal cheese-ripening, but the exact influence of varying quantities of acid upon the

chemical changes of the ripening process has not yet been fully studied.

Transient and Cumulative Products in Cheese-ripening.

In studying the influence of various conditions upon the chemical changes of the nitrogen compounds in the normal cheese-ripening process, we have noticed that the compounds grouped under the names paracasein, caseoses, and peptones, usually vary within comparatively narrow limi.s and do not appear to accumulate in the cheese in constantly increasing quantities. These compounds do not appear to show much definite regularity in the amounts formed under different conditions. On the other hand, amido compounds and ammonia accumulate in increasing amounts from the early age of the cheese during the whole process of normal ripening. The difference in the apparent behavior of these different classes of nitrogen compounds is most readily explained by regarding the compounds first formed in cheese-ripening as intermediate transient-products. Thus we find paranuclein, caseoses, and peptones present in the earliest stage of cheese-ripening, and they show a tendency to increase somewhat for a period of time and then decrease. Just what the chemical relation of these compounds is to paracasein, or to paracasein monolactate, we are unable to say. It is probable that the molecule of the proteid compound first splits into paranuclein and caseoses or some closely related compounds, and from one or both these classes of compounds are formed peptones. Whatever may be the precise chemical relation and order of formation, the point we wish to keep in mind is that the amounts of these compounds do not increase regularly or accumulate continuously in the cheese. The extent to which any accumulation occurs in these transient stages depends upon the conditions of ripening. For example, at low temperatures, the transient nitrogen products formed appear to pass into other forms less rapidly than at higher temperatures and they tend to accumulate to some extent. This can be shown by comparing the results secured with cheeses ripened at 32° F. and 70° F. These data are taken from Table II. :

Age of cheese.	Percentage of nitrogen in form of paranuclein in cheese at		Percentage of nitrogen in form of caseoses in cheese at		Percentage of nitrogen in form of peptones in cheese at	
	32° F.	70° F.	32° F.	70° F.	32° F.	70° F.
Months.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1.5	1.27	2.03	1.05	4.07	1.30	6.81
3	4.05	3.71	2.97	4.63	2.23	5.45
6	3.44	2.68	5.24	3.37	4.53	3.67
9	4.47	3.13	4.29	4.24	4.36	3.33
12	4.15	2.45	4.17	4.12	4.53	3.51
18	4.12	2.60	5.06	3.20	4.17	1.50

Now, quite different from the behavior of these compounds is that of amido compounds, which appear beyond question to result from the proteolysis of peptones, and of ammonia, which is formed from the decomposition of amides. Ammonia is an end-product and the amido compounds are end-products to a considerable extent in cheese normally ripened. They therefore accumulate in increasing quantities under all conditions that favor their formation.

Influence of Products of Proteolysis on the Cheese-ripening Process.

Attention has been called to the fact that chemical changes in the nitrogen compounds of cheese take place much more rapidly in the early stages of ripening than later. In our work we found that in the first three months of the eighteen-month period of study, over 65 per cent of the nitrogen was changed into the form of water-soluble compounds. How can we explain this observed fact that the rate of chemical change, as measured by the formation of water-soluble nitrogen compounds, decreases as the age of cheese increases? The most obvious explanation is associated with the generally observed fact that in fermentation changes the products of the process weaken the action of the ferment, often inhibiting it altogether. In cheese we have an accumulation of fermentation-products in the form of water-soluble nitrogen compounds and, apparently, they serve to diminish the action of the agents that cause the changes.

In this connection it is interesting to notice that the end-products, the amides, and ammonia appear to exert a stronger influence than do the other soluble nitrogen compounds in de-

creasing the action of the ripening agents. This is indicated
by the following data taken from Table I. :

Age of cheese. Months.	Percentage of nitrogen in form of paranuclein, caseoses, and peptones.	Percentage of nitrogen in form of amides and ammonia.	Monthly average rate of increase of soluble nitrogen compounds for 100 lbs. of nitrogen in cheese. Lbs.
1.5	9.05	11.44	15.0
3	13.66	16.81	6.3
6	12.71	23.48	2.1
9	12.17	31.27	2.4
12	11.63	33.79	0.4
18	....	37.00	0.4

Thus, it is seen that the first-formed products of cheese-
ripening, paranuclein, caseoses, and peptones, remain fairly
uniform, while the amides and ammonia continuously in-
crease.

Why Moisture Influences the Cheese-ripening Process.

We have seen that an increased moisture-content in cheese
favors more active chemical changes in the process of ripen-
ing. This may be due to one or both of two effects. First,
moisture in itself may favor the activity of the ripening fer-
ments. It is well known that moisture is necessary for the
action of ferments and that increase of moisture above a cer-
tain amount increases their action. Second, the presence of
increased amounts of moisture serves to dilute the fermenta-
tion-products and to that extent to counteract their unfavora-
ble effect.

In ordinary cheese-ripening there is a constant loss of mois-
ture, and this serves to make more concentrated the fermenta-
tion-products which are increasing at the same time the mois-
ture is decreasing. Accordingly, after three to six months,
difference in moisture appears from the results of our work to
exert a more marked influence upon the increased formation
of soluble nitrogen compounds than in the early stages of
ripening.

The Character of the Action of Rennet-Extract.

In Bulletin No. 233 of this Station the work of others has

been confirmed in showing that the active constituent of rennet is a peptic ferment and that the part performed in cheeseripening by rennet-extract is a peptic digestion, in which the
chemical changes are largely confined to the conversion of
paracasein monolactate into paranuclein, caseoses, and peptones, only small amounts of amides being formed.

The Relation of Acid in Cheese to Cheese-ripening.

In Bulletin No. 203, page 240, of this Station, we called attention to the fact that presence of acid in cheese favors the
action of enzymes in the cheese-ripening process. In this
JOURNAL, **28**, No. 6, Dec., 1902, it was shown that acid performs a specific function in the cheese-making process,
uniting with paracasein to form paracasein monolactate. It
was also shown that paracasein monolactate appears to form
the real starting-point of the cheese-ripening process, since
we have been unable to obtain soluble nitrogen compounds
to any extent without the presence of paracasein monolactate
and since this compound decreases in amount as soluble
nitrogen compounds increase.

From our work previously done, it appears that acid in
cheese is a prerequisite for its ripening. Additional work is
required to show the specific influence of different amounts of
acid upon the cheese-ripening process.

NOTE ON THE BUDDE EFFECT WITH REFERENCE TO BROMINE.

By B. PALMER CALDWELL.

In the course of some investigations attempting to solve the
problem of the increased chemical activity of chlorine in sunlight, we were led to try a few experiments with bromine.
As the work was interrupted in its preliminary stage, no conclusions were reached. In the meantime, several papers on
the same general subject by J. W. Mellor and Edward
John Russell have appeared in the Journal of the London
Chemical Society (1902). As these authors in their work
have devoted themselves to experiments with chlorine alone,

we have thought it well to put on record the results of a few of our experiments on the Budde effect with reference to bromine.

As we wished to get comparative results, the apparatus was as follows : The vessels containing the chlorine and bromine were glass bulbs of 500 cc. capacity, provided with gas inlet and outlet tubes, each bearing a stop-cock. These were immersed in a glass vessel of water in such a way that a layer of water, 62 mm. thick, separated them from the surrounding air. The gases were passed into the respective bulbs (the temperature being such as to gasify the bromine). Each bulb was then connected with a manometer containing, in some experiments saturated sodium chloride solution, in other cases concentrated sulphuric acid.

In these experiments the apparatus was set up in a partially darkened room. The source of light was a photographic flash-light cartridge[1] exploded at a distance of 30 cm. from the outside of the water jacket.

A mean of the results of two experiments (which did not vary greatly from each other) gives the expansion of the chlorine, as indicated on the manometer scale, three divisions ; the expansion of the bromine, fifty-four divisions.

The recovery of the original volume was not immediate, but extended through a period of three seconds on an average. As these experiments were of a preliminary nature, the results are not given as exact, but only approximate. The gases were not perfectly dry nor pure. Similar experiments with hydrogen, oxygen, and air gave an almost imperceptible momentary indication of disturbed volume conditions.

In other experiments ordinary florence flasks were used in the same way, and Beckmann thermometers were inserted in the gases. The rise in temperature was by no means such as to account for the changed volumes, especially in the case of bromine. The temperature, change of air, chlorine, and bromine did not differ very materially from one another.

Mellor's conclusion with regard to chlorine is :[2] " There is

[1] Eastman's Flash Cartridge, No. 2.
[2] J. Chem. Soc. (London), Trans., **81**, 129 (1902).

no experimental evidence to show that chlorine gas under the influence of light undergoes any change capable of appreciably affecting the chemical activity of that element towards hydrogen.'' Presumably, then, there is no evidence in favor of the dissociation of chlorine molecules into ions in the sunlight. The results with bromine indicate the same general fact. Chlorine shows so much greater increased activity in sunlight than does bromine, that it should be supposed, that if the increase in volume—the Budde Effect—were caused by ionization, then this phenomenon would be far more noticeable in the case of chlorine than of bromine. This is not the case.

Whether his second conclusion[1] that the Budde Effect is entirely caused by '' part of the energy absorbed by moist chlorine from sunlight being dissipated as heat'' is true or not, remains to be seen. If this were the case, then the temperature rise should be much greater in the case of bromine than of chlorine, and this is not in accord with our experiments.

TULANE UNIV. OF LOUISIANA,
 NEW ORLEANS, LA.,
 Nov. I, 1902.

REPORT.

Recent Advances in Our Knowledge of the Metals of the Platinum Group.

1897–1903.

It is now six years since the publication of the Bibliography of the Metals of the Platinum Group, in which the literature of these elements was brought down to the close of 1896. It is the purpose of this paper to review some of the more important advances which have been made since that time in this field.

The number of workers has not been large, chiefly due, doubtless, to the cost of the raw material, which precludes any extensive development along the line of technical chemistry, and which, except in the case of platinum itself, compels investigators to work with inconveniently small quantities of material. Yet the number of papers within our field since the beginning of 1897 is nearly two hundred.

There is little new to chronicle regarding the occurrence of

[1] *Loc. cit.*

platinum in nature. Localities and output have undergone comparatively little change. By far the greatest portion of platinum comes, as it always has, from Russia, and these workings are gradually becoming poorer, though more extensively worked. A few months ago the papers told of rich platinum placers discovered on a tributary of the Iss in the northern Uralian district, but this has not been confirmed.

Platinum in the form of sperrylite, $PtAs_2$, seems to be a constant accompaniment of the Sudbury, Ontario, nickel ores, and is concentrated in the matte to the extent of about 50 grams of platinum per ton of nickel.

The Tulameen district, in British Columbia, has been a small producer of platinum, and was in 1900 quite thoroughly studied by Prof. J. F. Kemp, of Columbia University. While the platinum there is widely disseminated, it is very sparsely distributed in the mother-rock and in a very finely divided condition, precluding the possibility of economic working by any of the methods at present in use. Prof. Kemp considers that there is little probability of extensive platinum placers being found in any but very old land areas which have been subjected to protracted denudation and concentration.

Platinum, in the form of sperrylite, and perhaps also native, has been reported from some of the Colorado mines, and also from Alaska. Unfortunately, gold miners have generally regarded platinum, as far as it has been noticed in their washings, as a nuisance, so that it is probable that large quantities of the metal have been overlooked and thrown away in gold placers.

Prof. Kemp has made a notable contribution to the literature of the occurrence of platinum in his "Geological Relations and Distribution of Platinum and Associated Metals," published in 1902 as Bulletin 193 of the United States Geological Survey. In this work Prof. Kemp has reviewed all the occurrences of platinum, treated those of the Tulameen district and of the Urals very fully, and discussed the geology of platinum deposits more completely than had previously been done. He inclines to the opinion that platinum has been deposited from fusion, contrary to the views of Meunier, who holds that the platinum is a later deposition. From a study of sections of platinum and gold nuggets, Liversidge[1] also concludes that these metals have been precipitated from aqueous solution.

It may not be out of place to state that I have, through the courtesy of Baker & Company, in my possession a specimen

[1] Proc. Chem. Soc. (London), **174**, 22 (1897).

of platinum sand which is well authenticated as having come from the southern part of the Appalachian system, but from what particular locality we have never been able to ascertain.

In connection with the working of platinum, as well as gold and silver deposits, a patent has been issued[1] in Germany to Frasch, who proposes to pump a solvent such as chlorine or bromine water, or potassium cyanide, directly into the natural alluvial deposits, thereby aiming to recover the fine particles which are lost in the tailings of ordinary washing.

During the period under our consideration no new element has been reported in the platinum group, and Mallet[2] has shown that the last proposed metal, davyum, has no claim to independent existence. Large quantities of platinum residues were placed by Sir George Matthey at Dr. Mallet's disposal, and using Kern's own methods, no indication of a new metal was found. In all probability Kern's davyum was merely a mixture of iridium and rhodium.

A few new forms of platinum apparatus have been devised. Stehman[3] has improved the Shimer crucible by using brass screws and asbestos packing instead of rubber for connections, avoiding the danger of organic matter falling into the carbon.

Soltsien[4] uses a narrow bent tube of platinum, after the manner of open tubes in blow-pipe analysis, for incineration in ash determinations.

Friedrichs[5] makes a very practical handle for a platinum spatula by fastening the end into a small porcelain tube by means of fused glass.

Probably most of us have suffered by the breaking off of the platinum eudiometer wires close to the glass. Palmaer[6] protects the wire by enclosing it in a small glass tube, fused on to the apparatus, and bent upward. A drop or two of mercury in the tube serves to make convenient connections.

Cowper-Coles[7] suggests that palladium is readily deposited electrolytically from ammonium palladium chloride solutions, and gives a better reflecting surface than silver, while it is as hard as nickel.

The Heraeus electric combustion-furnace promises to become useful. The resistance is furnished by a strip of very thin platinum foil wound spirally around the glass tube. Any desired temperature up to fusion can be rapidly obtained without danger of breaking the glass. Heraeus has also

[1] D. R. P. 93178.
[2] This JOURNAL, **20,** 776 (1898).
[3] J. Am. Chem. Soc., **25,** 237 (1903).
[4] Pharm. Ztg., **42,** 293 (1897).
[5] Chem. Ztg., **22,** 917 (1898).
[6] Ber. d. chem. Ges., **32,** 2570 (1899).
[7] Chem. News, **79,** 280 (1899).

made a crucible of pure iridium in which quartz can be fused for making quartz apparatus, by means of the oxyhydrogen blowpipe.

The demand for resistant electrodes has led to improvements by Heraeus.[1] He has found that without sacrificing the durability of the electrodes, a greatly increased surface area can be obtained by using the thinnest platinum or platinum-iridium foil. This is welded to platinum wire, which is enclosed in glass tubing. The platinum wire is in turn soldered to copper conductors. For large currents an indefinite number of these individual electrodes may be combined.

The ideal material for electrodes is considered by Foerster[2] to be a 10 per cent alloy of platinum with iridium. This can be used as thin as 0.0075 mm. and is available in salt solutions, with or without diaphragm. According to Denso[3] such electrodes can be used in the presence of free acid and at any temperature. There is at first a slight loss owing to impurities, but this is only temporary. Bran[4] finds there is less loss with high current density than with low. The proportion of iridium in the alloy within limits of a few per cent has no effect, but with as much as 25 per cent the durability of the electrode is increased.

By the action of the alternating current platinum electrodes are slowly carried into solution.[5] Ruer[6] considers that this is owing to the formation of an insoluble peroxide, which is reduced by the reversed current to a lower oxide, which enters the solution. In the case of such electrolytes as ammonia, potassium cyanide, etc., complex platinum salts are formed. Low results in the electrolytic determination of mercury are attributed by Glaser[7] to the fact that the platinum cathode is soluble in potassium cyanide. Under similar circumstances gold and silver are not soluble.

In 1900 an investigation was made by Hall[8] as to the loss of weight experienced by platinum on subjection to high temperatures. He attributes the loss to the formation of a volatile oxide. This has been further studied by Holborn[9] in conjunction with Henning and Austin, and extended to other metals and alloys of the group, and to other gases than air and oxygen. In these investigations the wire or foil was

[1] D. R. P. 132588.
[2] Ztschr. f. Elektrochem., **8**, 143 (1902).
[3] *Ibid.*, **8**, 147 (1902).
[4] *Ibid.*. **8**, 197 (1902).
[5] Margules : Wied. Ann., **66**, 540, 629 (1898).
[6] Ztschr. f. Elektrochem., **9**, 235 (1903).
[7] *Ibid.*, **9**, 11 (1903).
[8] J. Am. Chem. Soc., **22**, 494 (1900).
[9] Sitzber. Akad. Wiss.,Berlin, 1902, 936 ; 1903, 245.

electrically heated. In all cases more or less loss was sustained, the metals generally (except in the case of the iridium-rhodium alloy) became more flexible, and showe d a crystalline structure. Except in the case of iridium al loys, the loss was very small ; here, however, there was a decided loss, which diminished as more iridium had been removed from the surface. It is suggested that this loss could lead to errors in thermo-elements. The loss was generally greater in oxygen than in air, and was little in nitrogen. Where oxidizing atmospheres are present, the loss must be attributed to chemical action, but in hydrogen it is probably simply a sublimation of the metal. In this connection it is interesting to note that when ruthenium is heated to 1000° in oxygen it slowly volatilizes as RuO_4, being deposited as a lower oxide in the cooler portion of the tube, although RuO_4 itself is decomposed with explosive violence at about 100°.

In studying the composition of platinum which has become brittle by use, Hartley[1] shows by the use of the spectroscope the absence of all injurious elements but carbon and phosphorus, though it is difficult to prove the absence of iron from the platinum, owing to the closeness of their characteristic lines. Rosenhain,[2] however, attributes the brittleness of platinum to a recrystallization, at temperatures slightly below its fusion-point, similar to that experienced by other metals. White-hot platinum is easily shattered by a blow. The crystalline appearance of platinum which has been highly heated is not superficial, but extends into the mass. According to Heraeus,[3] the damage to platinum crucibles in phosphate analyses is due to the fact that magnesium phosphate is readily reduced by ammonia below 900° and by carbon below 950°.

The first mention I have been able to find of the use of metallic osmium to take the place of carbon in the filament of the incandescent electric light is in Merck's Jahresbericht for 1898 (page 25). Platinum early proved too fusible ; Poland tried iridium in 1890. Osmium is practically infusible by any ordinary current, but owing to the ease with which it is oxidized it must be used in a vacuum. It gives a whiter light than carbon and is more economical; since it can be run with a 25-volt current, it is advantageous for use with a storage battery.[4] The greatest and almost insuperable obstacle to its use is its cost. It should, however, be noted that osmium is the only constituent of osmiridium which has no

[1] Proc. Chem. Soc. (London), **18**, 30 (1902) ; Phil. Mag. [6], **4**, 84 (1902).
[2] Proc. Roy. Soc. (London), **70**, 252 (1902).
[3] Ztschr. angew. Chem., **15**, 917 (1902).
[4] Scholz : Jour. f. Gasbeleuchtung, **44**, 101 (1901).

practical use, if we except the insignificant amount of osmium
tetroxide used in microscopy ; and osmium composes nearly
one-half of osmiridium.   Various devices have been patented[1]
for preparing osmium filaments, and also for preparing com-
plex filaments of osmium alloys, of carbon impregnated with
osmium, or of rare earths mingled with osmium.   An osmium-
platinum alloy may be heated till the platinum volatilizes ;
platinum wire or a carbon filament may be heated in an at-
mosphere of osmium tetroxide till sufficient osmium is depos-
ited ; the rare earths may be made into a paste with osmium
sponge or some osmium compound, and then heated ; in any
case, when the osmium filament is heated to a high tempera-
ture by the current in a vacuum or in an indifferent gas it be-
comes a coherent metal.   It is said that ruthenium gives
much the same results as osmium, and can be similarly made
into filaments, but its excessive rarity would render its use
impracticable ; indeed, it hardly seems possible at present that
the osmium light should come into any general use.

No subject connected with the platinum metals has recently
attracted more attention than the work of Bredig and his fol-
lowers on colloidal platinum as an inorganic ferment.   In
1898 Bredig[2] published an account of a very finely divided
form of platinum prepared by passing a current of 6 to 10 am-
peres at 30 to 40 volts between platinum electrodes immersed
in water.   An apparent solution was obtained of a dark wine
color, which did not clear up in weeks and which was very
active in promoting those so-called catalytic actions which
had long been known to be brought about by finely divided
platinum in the form of sponge or platinum black.   It was
soon found that this solution, now known as colloidal plati-
num, possesses many of the properties of an organic ferment,
and, like the latter, is so affected by the presence of certain
salts and other substances that it is no strained application of
the term to speak of its being poisoned.[3]   This action was
tested by adding the '' poison'' to the colloidal platinum, then
adding hydrogen peroxide, and titrating the undecomposed
peroxide with potassium permanganate.   In the early experi-
ments it was found that prussic acid was an active poison to
the platinum, as were iodine, mercuric chloride, hydrogen
sulphide, and some other compounds.   Carbon monoxide,
phosphorus, and phosphine were very poisonous, but the
platinum soon recovered from their effect.   Arsenic, hydro-
chloric acid, oxalic acid, and ammonium chloride were mod-

[1] D. R. P. 132428, 138135, 140468 ; Abstracts in Chem. Centrbl., 1902, II : 83 ; 1903, I
209, 903.
[2] Ztschr. f. Elektrochem , **4**, 514 (1898).
[3] Bredig and Ikeda : Ztschr. phys. Chem., **37**, 1 (1901).

erately poisonous, while, so far from being injurious, formic acid, dilute nitric acid, and hydrazine might be said to have a healthy action. Alcohol, ether, and chloroform were inert. There is thus a strong similarity as regards the action of poisons upon this inorganic ferment and upon organic ferments, but by no means an identity. Raudnitz[1] considered the action due to the influence of the poison upon the catalyzed substance, pointing out that while the enzyme of milk has little effect upon hydrogen peroxide in the presence of prussic acid, the action is restored if the prussic acid be driven out by a current of air. Bredig,[2] however, holds that the poisoning is due to the action of the poison upon the catalyzer (catalyzing substance), pointing out that the analogy between organic and inorganic ferments must not be pushed too far. Sodium thiosulphate, for example, is a strong poison to the latter, but is not a poison to blood and enzyme catalysis. This work promises to throw much light upon the action of organic ferments. The action of colloidal platinum on mixtures of oxygen and hydrogen has been studied by Ernst,[3] and upon the persulphates by Price.[4] Gutbier[5] obtained a very sensitive platinum by the reduction of dilute chloroplatinic acid with hydrazine hydroxide.

Somewhat along this line are the studies of Höber[6] on the action of poisons on the oxyhydrogen cell, the electrodes being platinum foil saturated at one pole with hydrogen and at the other with oxygen Potassium cyanide and hydroxylamine poison only the oxygen pole, while ammonium sulphide and carbon bisulphide poison both poles. Corrosive sublimate poisons the platinum oxygen very slightly, but the platinum hydrogen strongly. The action is attributed by Höber to the formation of a complex platinum salt.

The successful solution of the problem of sulphuric acid manufacture by the contact process should be mentioned here, though most of the experimental work belongs to the earlier period. An active contact substance is prepared by Majert[7] by impregnating asbestos or some similar mass with a solution of platinum chloride in alcohol or other organic solvent, and burning off the solvent. A very active platinized asbestos may be thus obtained containing not over 2 per cent of platinum. A patent[8] has also been taken out for regenerating

1 Bredig and Ikeda : Ztschr. phys. Chem., **37,** 551 (1901).
2 *Ibid.*, **38,** 122 (1901).
3 *Ibid.*, **37,** 448 (1901).
4 Ber. d. chem. Ges., **35,** 291 (1902).
5 Ztschr. anorg. Chem., **32,** 347 (1902).
6 Pflüger's Arch., **82,** 631 (1900).
7 D. R. P. 134928.
8 D. R. P. 135887.

a contact substance which has been poisoned by arsenic, by driving steam through the contact mass with the chamber gases.

The relation of platinum and palladium to gases continues to attract attention, as it has since the discovery of platinum sponge by Doebereiner eighty years ago, and the work of Graham on palladium in 1868. Randall,[1] using special precautions, finds that hydrogen passes slowly through white-hot platinum, but that toward oxygen, hydrogen, and methane the metal is perfectly impervious. Dewar[2] failed to find a critical temperature for palladium-hydrogen, the gas still being absorbed by the metal at $500°$ under a pressure of 120 atmospheres. The heat of combination at high temperatures is greater than at low. The experiments of Mond, Ramsay, and Shields[3] have been continued and they conclude that the compound Pd_2H does not exist, though possibly Pd_3H_2 does. Zelinsky[4] finds zinc coated with palladium-hydrogen to be a good reducing agent for alkyl bromides and iodides, hydrocarbons being formed.

A little work has been done upon the alloys of platinum. Brunk[5] finds platinum slowly dissolved by aluminium and on treatment of the regulus with dilute hydrochloric acid, crystals having the apparent composition of Pt_3Al_{10} were obtained. From these the aluminium was almost completely dissolved by more concentrated acid. Hodgkinson, Waring, and Desborough[6] obtained, by heating in a vacuum, $PdCd_2$, but the alloys with zinc and with magnesium were of more doubtful composition. No definite compounds could be obtained with these metals and palladium.

The platinum-silver alloys have always interested assayers. That silver can be dissolved out completely by concentrated sulphuric acid is confirmed by Richards.[7] The rather surprising statement was presented by Spiller[8] to the London Chemical Society that from platinum-silver alloys containing from 0.25 per cent to 12 per cent platinum, the silver could be almost completely dissolved out with nitric acid of sp. gr. 1.2 to 1.42, hardly more than a trace of platinum going into solution. This was contrary to previous experience, and more recent unpublished experiments by Lodge, and in my own laboratory, show that while the weaker the acid and the

[1] This JOURNAL, 19, 682 (1897).
[2] Proc. Chem. Soc. (London), 183, 192 (1897).
[3] Proc. Roy. Soc. (London), 62, 290 (1897).
[4] Ber. d. chem. Ges., 31, 3203 (1898).
[5] *Ibid.,* 34, 2733 (1901).
[6] Chem. News, 80, 185 (1899).
[7] The Analyst, 27, 265 (1902).
[8] Proc. Chem. Soc. (London), 180, 118 (1897).

richer the alloy in platinum, the less platinum enters solution, no regularity can be established, and in no case does all the platinum remain undissolved. The explanation of these discrepancies is doubtless that suggested by Harcourt at the Chemical Society meeting, that Spiller's alloys were not complete solutions, having been formed at too low a temperature.

No simple or satisfactory method of assay for the platinum metals in conjunction with gold has been devised, though the subject has been studied by Vanino and Seemann,[1] Peterson,[2] Rössler,[3] and Mietzschke.[4]

The use of sodium peroxide promises to simplify the decomposition of iridosmium, which has always been a difficult problem. This agent has a powerful oxidizing action upon all the metals of the group, giving soluble compounds with all except platinum and rhodium. Dudley[5] has studied its action upon platinum, while Leidié and Quennessen[6] have applied the action of sodium peroxide, combined with the subsequent use of sodium nitrate, to the separation of the metals. Leidié[7] obtains pure iridium by a sodium nitrite method distinct from that of Gibbs. Jörgensen[8] purifies rhodium from iridium by the use of the chloropentaminerhodium salts. He finds the atomic weight of this purified rhodium to be the same as that heretofore determined, indicating that the previously obtained rhodium was not contaminated by iridium. Mylius and Dietz[9] have given a full description of methods of obtaining all the platinum metals in a state of purity.

For the preparation of barium platocyanide, Bergsöe[10] treats chloroplatinic acid with barium hydroxide and sulphur dioxide, and the resultant platosulphite with barium cyanide. Or the first mixture may be treated directly with sulphur dioxide after the addition of hydrocyanic acid. An output of 75 per cent is obtained and the platinum is perfectly free from iridium. It may be questioned, however, whether for the ordinary preparation of platocyanides this equals the method of dissolving platinum sulphide in a solution of alkaline cyanide.

A not uninteresting episode was the publication of a paper[11] by Sulč showing that osmium slowly lost weight when heated in the air at 212° and in oxygen at 170°, and the rejoinder by

[1] Ber. d. chem. Ges., **32**, 1968 (1899).
[2] Ztschr. anorg. Chem., **19**, 59 (1898).
[3] Chem. Ztg., **24**, 733 (1900).
[4] Berg Hütt. Ztg., **59**, 61 (1900).
[5] This JOURNAL, **28**, 59 (1902).
[6] Bull. soc. chim. [3], **25**, 9, 840 (1901) ; **27**, 179 (1902).
[7] J. Pharm. Chim. [6], **10**, 163 (1899).
[8] Ztschr. anorg. Chem., **34**, 82 (1903).
[9] Ber. d. chem. Ges., **31**, 3187 (1898).
[10] Ztschr. anorg. Chem., **19**, 318 (1899).
[11] *Ibid.*, **19**, 332 (1899).

Vèzes[1] that Deville and Debray long ago showed that osmium, when finely divided, slowly volatilizes as osmium tetroxide even at ordinary temperatures. The rapidity of this oxidation depends merely upon the fineness of the osmium.

Turning now to the halide compounds of platinum, Mallet[2] finds that platinum sponge precipitated by formaldehyde is, after exposure when damp to the air, somewhat soluble in rather strong hydrochloric acid. Méker[3] prepares the bromoplatinates by heating the metal with ammonium sulphate and a bromide to 350°. Very important is a new method discovered by Vèzes[4] of preparing potassium chloroplatinite, which comes as a great relief to those who have been used to preparing the salt, for photographic and other purposes, by reducing the chloroplatinate with cuprous chloride, sulphur dioxide, or even by heat. In his work on the platoxalates, Vèzes found that by boiling the chloroplatinate suspended in water with the calculated amount[5] of potassium oxalate for several hours, it is quantitatively converted into the chloroplatinite. A large portion of the salt crystallizes out on cooling, while the balance may be recovered by evaporation and precipitation with alcohol.

In 1878 Pitkin[6] prepared a supposed mixed haloplatinate by the addition of potassium bromide to chloroplatinic acid. This was shown by Herty[7] and others to be an isomorphous mixture. Miolati[8] has, however, prepared a true bromochloroplatinate by the addition of bromine to potassium chloroplatinite. Its composition is $K_2PtCl_4Br_2$. I have myself found that when hydrogen bromoruthenite is precipitated by potassium chloride, potassium bromoruthenite, K_2RuBr_5, is formed, free from chlorine.

The use of chloroplatinic acid in potash determinations has been studied by Atterberg[9] and Rohland,[10] with no suggestions of a change from the ordinary procedure. The residues from analysis are treated for the recovery of platinum with aluminium turnings by Wiley,[11] with magnesium by Atterberg,[12] and with zinc dust by Berthold.[13] Knoevenagel and Ebler[14] find

1 Ztschr. anorg. Chem., **20**, 230 (1899).
2 This JOURNAL, **25**, 430 (1901).
3 Compt. rend., **125**, 1029 (1897).
4 Bull. soc. chim. [3], **19**, 879 (1898).
5 100 grams K_2PtCl_6, 37 grams $K_2C_2O_4.H_2O$, suspended in 1 liter of water.
6 J. Am. Chem. Soc., **1**, 472 (1878) ; **2**, 296, 408 (1879).
7 *Ibid.*, **18**, 130 (1896).
8 Ztschr. anorg. Chem., **14**, 237 (1897).
9 Chem. Ztg., **22**, 522, 538 (1898).
10 Ztschr. anorg. Chem., **15**, 412 (1897) ; **16**, 305 (1898).
11 J. Am. Chem. Soc., **19**, 258 (1897).
12 *Loc. cit.*
13 Ztschr. angew. Chem., **14**, 621 (1901).
14 Ber. d. chem. Ges., **35**, 3055 (1902).

that hydrazine precipitates platinum completely in caustic soda or acetic acid solutions, but incompletely in the presence of ammonia or a mineral acid. Hydrogen peroxide does not precipitate it at all, nor does hydroxylamine, except a partial precipitation in ammoniacal solutions.

In their remarkable work upon the basic properties of nitrogen, Baeyer and Villiger[1] use chloroplatinic acid as a weak acid to form salts with oxygen bases, and suggest that cyanoplatinic acid, $H_2Pt(CN)_4$, can probably be similarly used. The compound formed when hydrochloric acid acts upon an alcoholic solution of potassium cyanoplatinite seems to be a salt, $2C_2H_5OH, H_2Pt(CN)_4$, in which alcohol plays the part of a base.

By far the most interesting chapter of the work upon the platinum halides is that which has been most largely developed by Miolati on the different chloroplatinic acids, and the discovery of which we owe almost exclusively to modern physico-chemical methods. In 1870 S. A. Norton[2] described a new chloride of platinum, $PtCl_4.5H_2O$. In 1898 Sonstadt[3] studied the action of a large amount of water upon chloroplatinic acid. He found that in hot water decomposition takes place with the formation of a chloride of platinum, $PtCl$. This change he later[4] found to take place in cold water under the influence of light. The same year Kohlrausch[5] noted that the solution of Norton's tetrachloride acted as an electrolyte, and suggested that there seemed to be formed an acid, H_2PtCl_4O. The next year this acid was carefully investigated by Hittorf and Salkowski[6] and its existence confirmed by the preparation and analysis of its silver salt. In 1900 Kohlrausch[7] studied further the hydrolysis of both chloroplatinic acid and Norton's tetrachloride, and Dittenberger and Dietz[8] considered that the tetrachloroplatinic acid, H_2PtCl_4O, was decomposed into the ordinary hexachloroplatinic acid and a compound $PtCl_2O$.

The subject was now taken up by Miolati, partly in conjunction with Bellucci. In his first article[9] he gives a resumé of the matter, showing that the true tetrachloroplatinic acid has the formula $H_2PtCl_4(OH)_2$, describes the silver, zinc, cadmium, thallium, and lead salts, and then goes on to show the great probability that numerous other derivatives and de-

[1] Ber. d. chem. Ges., **34**, 2679 (1901) ; **35**, 1201 (1902).
[2] J. prakt. Chem. [2], **2**, 469 (1870) ; **5**, 365 (1872).
[3] Proc. Chem. Soc. (London), **188**, 25 (1898).
[4] *Ibid.*, **198**, 179 (1898).
[5] Ann. phys. Chem. [2], **63**, 423 (1898).
[6] Ztschr. phys. Chem., **29**, 546 (1899).
[7] *Ibid.*, **33**, 257 (1900).
[8] Ann. phys. Chem. [2], **68**, 853 (1899).
[9] Miolati : Ztschr. anorg. Chem., **22**, 445 (1900).

composition-products of the hexachloroplatinic acid are in reality to be considered as various members of a series of acids, all derived from the ordinary chloroplatinic acid, H_2PtCl_6, by the replacement of one or more atoms of chlorine by the hydroxyl group. These he calls the mono-, di-, tri-, etc., chloroplatinic acids. Jörgensen's $PtCl_2O.H_2O$ is an anhydride of dichloroplatinic acid; the well-known precipitate formed by the action of lime-water on chloroplatinic acid in the sunlight is the calcium salt of monochloroplatinic acid. In the hands of these two chemists the work rapidly developed until now salts of each member of the series have ʋeen prepared with the exception of the trichloroplatinic acid; salts of trichloroplatinous acid, H_2PtCl_3OH, have, however, been formed. Several of the other haloplatinic acids have also been made.

Pentachloroplatinates[1] are derived by the action of fused caustic potash upon hexachloroplatinic acid; monochloroplatinates[2] by lime-water, as above, dichloroplatinates[3] by the action of ammonia on tetrachloroplatinic acid; trichloroplatinites[4] by the evaporation of tetrachloroplatinous acid in a vacuum; tetrabromoplatinates[5] and tetraiodoplatinates[6] similarly to the chlorine salts. Efforts have been made by Miolati and Bellucci[7] to prepare similar salts where the halides are replaced by other groups, but they have thus far failed. Halocyanates such as $Ag_2Pt(CN)_4Cl_2$, and halonitrites, as $K_2Pt(NO_2)_4Br_2$, have, however, been obtained. These are similar to the complex platinum salts of Vèzes, shortly to be considered.

To this may be added the work of de Coninck[8] on another form of decomposition of platinum chloride, by filtration through animal charcoal, or by the action of such salts as magnesium sulphate in sunlight.

During the past six years Prof. Vèzes, of the University of Bordeaux, has given much time to the investigation of the complex platinum acids. If potassium platonitrite (to use the old nomenclature), $K_2Pt(NO_2)_4$, is treated with oxalic acid, the platooxalate is obtained. This reaction proceeds in two stages, and the intermediate product, the platooxalonitrite, $(K_2PtOx(NO_2)_2.H_2O)$, is easily prepared.[9] This reaction may be used practically to separate platinum from all the

1 Miolati and Bellucci : Ztschr. anorg. Chem., **24**, 209 (1901).
2 Bellucci : Atti. R. Accad. Lincei, Roma [5], **11**, II, 241. 271 (1902).
3 Miolati and Pendini : Ztschr. anorg. Chem., **33**, 251 (1903).
4 Miolati and Pendini : *Ibid.*, **33**, 264 (1903).
5 Miolati and Bellucci : *Ibid.*, **24**, 222 (1901).
6 Bellucci : Atti R. Accad. Lincei, Roma [5], **11**, I, 8 (1902).
7 Gazzetta, **30**, II, 588 (1901).
8 Compt. rend., **130**, 1551 (1900) ; Bull. Acad. Roy. Belg., 1902, 730.
9 *Ibid.*, **125**, 525 (1897) ; Bull. soc. chim. [3], **21**, 481 (1899).

other members of the group. The salts of the alkalies and alkaline earths were obtained, as well as a double potassium barium salt.[1] The salts of the heavy metals decompose at once into the oxalates, and the free acid itself is too unstable to be obtained by evaporation.[2] The reaction between the platonitrites and potassium oxalate on the one hand, and the platooxalate and potassium nitrite upon the other, is a reversible reaction. The same is true where the platinum-chloronitrite $(K_2PtCl_2(NO_2)_2)$ is substituted for the simple platonitrite.[3] The same is again true of the reaction in passing from the chloroplatinite to the platooxalate by the addition of potassium oxalate.[4] I have found a similar reaction between the chlororuthenite and oxalic acid, which has thus far negatived my efforts to separate the ruthenooxalate. It was in connection with his work upon these oxalates that Vèzes recognized that the first action of potassium oxalate upon chloroplatinates is that of reduction to the chloroplatinites, which has already been noted in connection with the preparation of the latter salt.

In 1893 Vèzes found that if a solution of a platonitrite be acidified and warmed, a peculiar salt is formed which is copper-red in color, but gives an almost colorless solution. This reminds one of the so-called platoplaticyanides of Knop and Schnedermann, which are formed by the addition of a trace of an oxidizing material, such as chlorine, to a concentrated solution of platocyanide. The constitution of these cyanides was cleared up by Hadow, who showed that they are a combination of 5 molecules of a platocyanide with 1 molecule of a platicyanide. Werner anticipated that Vèzes' red platinonitrite would prove to have a similar composition, but its analysis shows it to have the formula $K_2H_4Pt_3O(NO_2)_6$, which seems to indicate a reduction rather than an oxidation.[5] Meantime Miolati[6] has obtained a similar or identical red salt by the dry heating of addition-products, $K_2Pt(NO_2)_4,N_2O_4$ and $K_2Pt(NO_2)_4,HCl$, of the platinonitrite, and Vèzes himself[7] has obtained similar salts in the attempt to form platonitrites of copper.

In studying the platooxalates, Werner[8] has found two classes of salts, one yellow and the other dark-red, and suggests the possibility of stereoisomerism.

[1] Bull. soc. chim. [3], **27**, 157 (1901).
[2] *Ibid.* [3], **29**, 83 (1903).
[3] *Ibid.* [3], **21**, 143 (1899).
[4] Ann. chim. Phys. [7], **15**, 444 (1898).
[5] Vèzes : Ztschr. anorg. Chem., **15**, 278 (1897).
[6] Atti R. Accad. Lincei, Roma [5], **5**, II,,355 (1896).
[7] Bull. soc. chim. [3], **27**, 930 (1902).
[8] Ztschr. anorg. Chem., **21**, 377 (1899).

Some little work has been done during the last few years upon the platinum bases, but little has been added to our knowledge of the constitution of these interesting compounds. Two papers have appeared on the subject from Jörgensen,[1] which reveal the fact that he still remains antagonistic to the views of Werner. He has changed his opinion in one particular, in that he now considers Peyrone's base to possess the symmetrical formula, $Pt\begin{smallmatrix} NH_3Cl \\ NH_3Cl \end{smallmatrix}$, while Reiset's second chloride is the symmetrical form, $Pt\begin{smallmatrix} NH_3.NH_3Cl \\ Cl \end{smallmatrix}$. He also draws interesting analogies between these bases and the ethylene bases (acechlorplatin, etc.) of Zeise. Prandtl and Hofmann[2] and Bülmann[3] have also worked along this line, the former making the ethylene base by the action of chloroform on chloroplatinic acid, and the latter forming similar compounds with allyl alcohol. Werner[4] has prepared a series of acetylacetone compounds; while Uhlenhuth[5] obtains with hydroxylamine two isomeric bases of the formula

$$Pt(NH_2OH)_2Cl_2$$
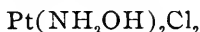
as well as a tetrahydroxylamine base. Cossa,[6] who also adheres to the Blomstrand theory of the constitution of the platinum bases, presents a paper on the missing member of the amine series, that in which but a single ammonia group is present, and has prepared a number of derivatives of the chloride. While he has not succeeded in isolating the chloride itself, he has prepared the thiocyanate, $Pt(NH_3)(SCN)_2$.

The most important paper upon this subject is that of Klason,[7] who treats the bases at length, both from a theoretical and an experimental standpoint. He considers the ammonia to be present in two forms, in one of which it is united solely to the platinum atom and in the other to both platinum and the negative element or group; the former class he distinguishes by the prefix "an." This is analogous to the linking of oxygen to carbon in the carbonyl group, while the other form would resemble the oxygen in the hydroxyl group. This classification and nomenclature then becomes the following :

[1] Ztschr. anorg. Chem., **24**, 153 (1900) ; **25**, 253 (1900).
[2] Ber. d. chem. Ges., **33**, 2981 (1900).
[3] *Ibid.*, **33**, 2196 (1900).
[4] *Ibid.*, **34**, 2584 (1900).
[5] Ann. Chem. (Liebig), **311**, 120 (1900).
[6] Ztschr. anorg. Chem., **14**, 367 (1897).
[7] J. prakt. Chem. [2], **67**, 1 (1903).

Class I.   1. NH_3PtCl_2.   Platosemianamine chloride.

          2. $ClPtNH_3Cl$.   Platosemiamine chloride.

Class II.   1. $(NH_3)_2PtCl_2$.   Platoanamine chloride.

          2. $NH_3Pt\underset{\displaystyle Cl}{\overset{\displaystyle NH_3Cl}{<}}$.   Platosemianaminesemiamine chloride.

          3. $Pt(NH_3Cl)_2$.   Platoamine chloride.

Class III.   1. $(NH_3)_2Pt\underset{\displaystyle Cl}{\overset{\displaystyle NH_3Cl}{<}}$.   Platoanaminesemidiamine chloride.

          2. $NH_3Pt(NH_3Cl)_2$.   Platosemianaminediamine chloride.

Class IV. $(NH_3)_2Pt(NH_3Cl)_2$.   Platodiamine chloride.

How this new aspirant for favor will be received by the respective advocates of the Blomstrand and the Werner theories remains to be seen, and what is more important, how it will explain the numerous mixed compounds and isomers of the group. Klason[1] himself has already applied it successfully to mixed platophosphinamine isomers.

Among the few remaining papers on platinum which we find in this period are one by Hofmann and Rabe[2] on derivatives of platinum mercaptides ; one by Müller,[3] who finds carbon monoxide has no action on the platocyanides ; one by Granger,[4] who forms three definite phosphides of platinum, Pt_3P_5, Pt_2P, and PtP_2, by heating phosphorus and platinum in an atmosphere of carbon dioxide ; one by Roessler,[5] who has prepared three tellurides, Pt_2Te, $PtTe$, and $PtTe_2$; one by Harbeck and Lunge,[6] who find that both platinum and palladium absorb carbon monoxide, probably forming compounds, and hence cannot be used in gas analysis to convert ethylene into ethane if carbon monoxide be present ; and, finally, a recommendation by Valenta[7] to improve the platinum toning-bath by the addition of an equal quantity of a 1 per cent solution of metaphenylenediamine.

Turning now to the other metals of the platinum group, one cannot but deplore the small amount of work which has been done, for, though the elements are rare and expensive, it is by work upon just such rare elements that we may hope for the greatest additions to our knowledge of chemical compounds in general. This applies, of course, equally well to our lack of any considerable knowledge of such elements as

[1] J. prakt. Chem. [2], **67,** 41 (1903).
[2] Ztschr. anorg. Chem., **14,** 293 (1897).
[3] Bull. soc. chim. [3], **29,** 27 (1903).
[4] Compt. rend., **123,** 1284 (1896).
[5] Ztschr. anorg. Chem., **15,** 405 (1897).
[6] *Ibid.,* **16,** 50 (1897).
[7] Phot. Corr., 1899.

columbium, tantalum, uranium, tungsten, tellurium, molybdenum, vanadium, titanium, indium, and perhaps some others. I can make no better suggestion to a young chemist than to take up one of these elements as a life study.

Beginning with palladium, we find that Vèzes[1] has extended his work on platinum oxalates to this metal, obtaining palladooxalates by similar reactions from both chloride and nitrite, and Loiseleur[2] has prepared the free palladooxalic acid, $H_2PdOx_2.6H_2O$. Intermediate compounds, as the oxalonitrites, were not found by them, but Rosenheim and Itzig[3] have, however, obtained not only oxalonitrites but also iodonitrites, and a peculiar chlorosulphite of the formula

$$(NH_4)_3PdCl_3SO_2.H_2O.$$
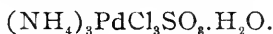
This seems to be a salt of mixed chloropalladous and pal-ladosulphurous acid, H_2PdCl_3 $\diagup$ SO_3H , an interesting combination.

The distinct yellow orthorhombic crystals of potassium palladonitrite are used by Pozzi and Couquet[4] for the purpose of detecting palladium in microchemical reactions.

Rosenheim and Maas[5] have prepared several pyridine palladi bases by the action of the halogens on the pallado base, while Kurnakow[6] has studied the palladoethylenediamine bases, as well as those of thiocarbamide.

The aniline, pyridine, quinoline, and piperidine bases have been prepared by Hardin,[7] and the first-mentioned was used for the atomic weight determination of palladium. The results obtained give the figure 107.014, which is slightly higher than that of most previous determinations. Fink[8] has examined the action of carbon monoxide on palladous chloride and finds three compounds, $PdCl_2,CO$, $2PdCl_2,3CO$, and $PdCl_2,2CO$, resembling the corresponding platinum compounds. In conclusion, it may be noted that palladous chloride has been recommended by Cohen[9] as a remedy for tuberculosis.

In the study of rhodium, Jörgensen[10] has continued his papers upon the constitution of the cobalt, chromium, and

[1] Bull. soc. chim. [3], **21**, 172 (1899).
[2] Compt. rend., **131**, 262 (1900).
[3] Ztschr. anorg. Chem., **23**, 28 (1900).
[4] Compt. rend., **130**, 1073 (1900).
[5] Ztschr. anorg. Chem., **18**, 331 (1898).
[6] *Ibid.*, **22**, 384 (1900).
[7] J. Am. Chem. Soc., **21**, 943 (1899).
[8] Compt. rend., **126**, 646 (1898).
[9] Pharm. Ztg., **46**, 131 (1901).
[10] Ztschr. anorg. Chem., **14**, 404 (1897) ; **16**, 184 (1898); **19**, 109 (1898).

rhodium bases, but his attention has been largely devoted to combatting the views of Werner. In one of the latest papers before his death, Joly,[1] to whom we owe so much of our knowledge of the chemistry of the platinum metals, in conjunction with Leidié, described a number of salts formed by heating the double rhodium nitrites, in which the rhodium oxide, RhO_2, acts as an acid-forming oxide, thus bringing the metal in this respect into line with iridium and the other metals of the group. The salts formed were $K_2O,6RhO_2$. $6-8H_2O$, $Na_2O,8RhO_2.11-12H_2O$, and $BaO,12RhO_2.15-16H_2O$. Leidié[2] has prepared the potassium rhodicyanide, $K_3Rh(CN)_6$, isomorphous with the corresponding ferri-, cobalti-, mangani-, and chromicyanides. He[3] has also prepared the anhydrous rhodium trichloride, $RhCl_3$, by heating the corresponding double salts at 440° in a current of dry hydrochloric acid. By heating ammonium chloroiridate similarly in dry chlorine, he gets the iridium trichloride, $IrCl_3$.

Along this line the most noteworthy piece of work is the preparation of the series of rhodium alums by Piccini and Marino,[4] and of the rubidium iridium alum by Marino.[5] Heretofore, indium has been the only element with an atomic weight greater than 59 from which alums have been formed, but the introduction of iridium to the list shows that the formation of alum is not, as has been supposed by many. a property exclusively of elements of low atomic weight. This opens a large field in which we may expect further results from Piccini, who has already so broadened our knowledge of this interesting class of double salts.

The only other work to chronicle under iridium is a further examination of the iridonitrites by Leidié,[6] the preparation of a series of iridochloronitrites, of formula $K_3IrCl_4(NO_2)_2$, by Miolati and Gialdini,[7] and a continuation of the studies of the iridiumamine bases by Palmaer.[8]

This brings us to the two remaining, and in some respects the most interesting, metals of the group, osmium and ruthenium. Osmiamic acid has attracted the attention of chemists since the days of Fritsche and Struve, its discoverers. Joly, after his elucidation of the nitrosoruthenates, considered osmiamic acid also to be a nitroso compound, assign-

[1] Compt. rend., **127**, 103 (1898).
[2] *Ibid.*, **130**, 87 (1900).
[3] *Ibid.*, **129**, 1249 (1899).
[4] Ztschr. anorg. Chem., **27**, 62 (1901).
[5] Gazz. chim. ital., **32**, II, 513 (1903).
[6] Ann. chim. Phys. [7], **26**, 479 (1902).
[7] Gazz. chim. ital., **32**, II, (1903).
[8] Ztschr. anorg. Chem., **13**, 211 (1896).

$$\overset{O}{\underset{\big/\big/}{}}$$

ing it the constitutional formula of HOOs—NO, in other words, a nitrosoosmous acid. This formula and constitution was confirmed by Brizard.[1] This is, however, questioned by Werner and Dinklage,[2] who obtain on treating the osmiamates with hydrochloric acid, salts of what they call nitrilopentachloroosmic acid, $K_2(OsNCl_5)$. They consider that os-

$$HN{=}\overset{\overset{\textstyle O\quad\ \ O}{\diagdown\;\;\big/\big/}}{Os}{=}O$$

miamic acid has the formula HN=Os=O, that is, it is the imine of osmium tetroxide, but that the salts have the tauto-

$$RO{-}\overset{\overset{\textstyle O\quad\ \ N}{\diagdown\;\;\big/\big/\big/}}{Os}{=}O$$

meric formula RO—Os=O. I cannot help feeling that this diagnosis of the case is a little doubtful, the more so as the formation of osmiamic acid from osmium tetroxide seems to be the result of reduction.

Rosenheim[3] alone, and in conjunction with Sasserath, has obtained a rather remarkable series of complex osmium sulphites and another of osmium chlorosulphites. By treatment of one of these salts with hydrochloric acid he obtains Na_6OsCl_{12}, which must be considered as sodium chloroorthoosmite, the chlorine derivative of the hypothetical orthoosmic acid, $Os(OH)_6$. This salt is almost, if not entirely, unique, and if Werner's views are true, would present a rather crowded co-ordinated group as the nucleus of the molecule.

The most important work on osmium is the thesis of Wintrebert,[4] which has been in part published from time to time in the French journals.[5] Much space is given to methods of analysis. In many cases the determination of the osmium was carried out by filtration through a peculiar form of Gooch tube, from which the osmium could be removed by heating in a current of air or oxygen. This permits the ready analysis of the silver salts. No worker on osmium should overlook this work. Wintrebert has prepared series of osmyl nitrites, osmyl halides, osmyl oxalates, and osmyl sulphites, of which the osmyl chloride, $K_2OsO_2Cl_4$, may be taken as a type, corresponding to the so-called oxychlororuthenites, $Cs_2RuO_2Cl_4$, previously prepared by me ; a series of osmyloxy-salts, including chloride, bromide, oxalate, and nitrites, of which

[1] Bull. soc. chim. [3], **21**, 170 (1899).
[2] Ber. d. chem. Ges., **34**, 2698 (1901).
[3] Ztschr. anorg. Chem., **21**, 122 (1899) ; **24**, 420 (1900).
[4] L. Wintrebert : Thesis, University of Bordeaux, Paris, 1902.
[5] Compt. rend., **131**, 264 (1900) ; **132**, 824 (1901) ; Bull. soc. chim. [3], **27**, 569 (1902) (with Vèzes) ; Ann. chim. Phys. [7], **28**, 15 (1903).

$(NH_4)_2OsO_3Cl_2$ is an example ; a series of bromosmates and iodoosmates corresponding to the chloroosmate, K_2OsCl_6 ; a series of nitrosochloroosmates, bromoosmates, and iodoosmates, of which $K_2Os(NO)Cl_5$ is one, corresponding to the nitrosoruthenates ; and finally an osmonitrite of the formula $K_2Os(NO_2)_5$, analogous to Joly's ruthenonitrite, $K_2Ru(NO_2)_5$. The whole thesis is a remarkable piece of work.

There have been several workers upon ruthenium in the last six years. Brizard[1] continued the work of Joly upon the nitrites, preparing several derivatives of the nitroso compounds $Ru_2H_2(NO)Cl_3$ and $Ru_2H_2(NO)Cl_5$, reduction-products of the ordinary nitrosochlororuthenate. Miolati and Tagiuri[2] consider that when chlorine acts upon a mixture of ruthenium and potassium chloride, the chlororuthenate, K_2RuCl_6, is first formed, but this breaks up into the hydrated chlororuthenate, $K_2RuCl_5.H_2O$, and this, in turn, on evaporation loses its water, becoming the ordinary chlororuthenite, K_2RuCl_5. They have also formed several sulphites and nitrososulphites. Several papers have been published by Antony and Lucchesi. They obtain ruthenium thiosulphate[3] by the action of sulphur dioxide upon ruthenic sulphate, $Ru(SO_4)_2$; by the careful solution of potassium ruthenate, (K_2RuO_4), in hydrochloric acid[4] and evaporation in a vacuum-desiccator, they obtain the long sought for potassium chlororuthenate, K_2RuCl_6 ; they form the ruthenic sulphate, $Ru(SO_4)_2$, by the action of sulphuric acid on barium ruthenate ; a sulphite,[5] $Ru_2(SO_3)_3$, is obtained ; and the two sulphides,[6] RuS_3 and RuS_2, are prepared by the action of hydrogen sulphide upon the chlororuthenate. This trisulphide has been also obtained by me, by the action of hydrogen sulphide on potassium ruthenate.

My own work upon ruthenium during the past six years has been largely devoted to the halide compounds,[7] though some work upon the ruthenocyanides,[8] partly in conjunction with H. D. Campbell, established their almost complete isomorphism with the corresponding ferrocyanides.

By the solution of potassium ruthenate, K_2RuO_4, or ruthenium tetroxide, RuO_4, in hydrochloric acid, under ordinary circumstances the chlororuthenite, K_2RuCl_5, is formed, the chlororuthenate, K_2RuCl_6, being very unstable. If, however, caesium or rubidium chloride be present, the intermediate oxychlororuthenate, $Cs_2RuO_2Cl_4$, can be obtained, a salt de-

[1] Compt. rend., **129**, 472 (1899) ; Ann. chim. Phys. [7], **21**, 311 (1900).
[2] Gazz. chim. ital., **30**, II, 511 (1901).
[3] *Ibid.*, **28**, II, 139 (1898).
[4] *Ibid.*, **29**, I, 312 (1899) ; **29**, II, 82 (1899).
[5] *Ibid.*, **30**, II, 71 (1900).
[6] *Ibid.*, **30**, II, 539 (1901).
[7] J. Am. Chem. Soc., **23**, 775 (1901).
[8] *Ibid.*, **18**, 981 (1896) ; **20**, 29 (1898).

composing instantly in water, and corresponding to Wintrebert's osmyl chloride. Hydrochloric acid changes this into the chlororuthenate or chlororuthenite, probably according to the temperature used. Under some conditions the chlororuthenate can be obtained directly by the action of ruthenium tetroxide on a solution of caesium chloride in hydrochloric acid, and this was my first preparation of the salt.

When a chlororuthenite is boiled with dilute alcoholic hydrochloric acid it is converted into a much more stable salt containing 1 molecule of water, $K_2Ru(H_2O)Cl_5$. This water is removed only at 180° and leaves a chlororuthenite, K_2RuCl_5, entirely different in properties from the ordinary chlororuthenite, with which it is isomeric. This salt, which, for want of a better name, I have denominated "aquo"-chlororuthenite, is itself isomeric with Miolati's hydrated chlororuthenite, but bears no resemblance to it in properties. When chlorine is added to the "aquo" salt, the chlororuthenate, K_2RuCl_6, is formed, corresponding in properties to the caesium and rubidium chlororuthenates previously prepared by me. It is quite distinct in its properties from the chlororuthenate described by Antony, so that there appears here again to be a case of isomerism. More recently I have prepared a number of bromine derivatives, which resemble closely the chlorides in their property of forming "aquo" salts, which in turn seem capable of uniting with bromine to form bromoruthenates. What the nature of the "aquo" salts may be is at present wholly a matter of conjecture. They seem to be much more ready to undergo reactions than the ordinary salt, as is shown by their union with chlorine, and by the fact that they act much more readily with oxalic acid than the ordinary salt to form oxalates.

The most striking point to me in this survey of the recent additions to our knowledge of the metals of the platinum group is not what has been attained, but rather the great field before us, upon which we have as yet hardly entered.

JAS. LEWIS HOWE.

REVIEWS.

DIE HERSTELLUNG DER AKKUMULATOREN. Von F. GRÜNWALD. Dritte Auflage. Verlag von W. Knapp. Halle a. S.

The author presents a "guide" to the construction, maintenance, and operation of the storage cell. While intended primarily for electrical engineers, it contains much more of the chemistry and electrolysis of the accumulator than is

usual in a book of this class. The treatment is restricted to the lead peroxide-sulphuric acid cell, which is shown to be a peculiar case of the primary cell from a consideration of the potential series of the metals in sulphuric acid. There is a general treatment of the electrochemistry of the primary cell, which is shown to be reversible in the particular case of the lead-lead peroxide cell. The electrolysis of sulphuric acid is discussed with the influence thereon of change of resistance due to changes of temperature and concentration, current density, migration of the ions, and polarization or counter currents, due to a change in nature of the electrodes. There is a chapter and table giving the electrolysis of the various sulphuric acids, and various compounds of lead with acids of this class. The value of porous electrodes is treated, and the physical and chemical properties of the raw materials, lead, the lead compounds, and sulphuric acid are given at some length.

The composition and method of mixing and applying the paste to the electrodes is given in detail.

The description of the various types of cell is limited to those of German manufacture.

There are complete instructions with examples for the installation and operation of batteries for various capacities and conditions of service.

The size of the volume is convenient, the illustrations are good, there are several convenient tables, but there is no index.   J. B. W.

RADIUM AND OTHER RADIO-ACTIVE SUBSTANCES; POLONIUM AND THORIUM, WITH A CONSIDERATION OF PHOSPHORESCENT AND FLUORESCENT SUBSTANCES, THE PROPERTIES AND APPLICATIONS OF SELENIUM AND THE TREATMENT OF DISEASE BY THE ULTRA-VIOLET LIGHT. By WILLIAM J. HAMMER, Consulting Electrical Engineer. New York : D. Van Nostrand Company. 1903. 8vo. pp. viii + 72.

This is a lecture delivered at a meeting of the American Institute of Electrical Engineers and the American Electrochemical Society, in New York, April 17, 1903. The lecture was profusely illustrated and an attempt is made to give the reader of the book an idea of the experiments performed and specimens exhibited. To quote from an introductory note : " The author of this paper has endeavored to exemplify certain fundamental principles connected with the phenomena upon (*sic*) which he has treated ; and in considering these subjects, all of which may be said to be on the borderland of science, to bring out by means of experiments, lantern slides, and illustrations which accompany the paper the practical and commercial side." " The practical and commercial side" of

radium and polonium is good. This recalls the remark that has recently gone the rounds of the newspapers : '' It is utter foolishness to pay $1,500,000 for 8 oz. of radium when you can get the same quantity of polonium for $1,000,000, which will answer just as well for almost all domestic purposes.''

Although Mr. Hammer's book is badly put together and is inexcusably bad from the literary as well as the purely scientific point of view, it is interesting and valuable. The author has been in communication with many of the investigators of whose work he attempts to give an account, and this gives freshness to the presentation though it also gives the impression of a certain amount of egotism on the part of Mr. Hammer. On page 19 he says : '' The tiny brown bulb which I hold in my hand is the duplicate of the one which Prof. Curie showed me at his laboratory last Fall, which contained the only sample of chemically pure radium in the world.'' On the preceding page occurs this passage : '' In a letter recently received by the author from Prof. Curie bearing upon the question of heat given off by radium Prof. Curie writes as follows : '' Since the time I had the honor to see you at our school of physics and chemistry I have continued to investigate into the radio-activity induced by radium and the way that radio-activity is disappearing in the course of time.''

'' In a study of another kind (in collaboration with M. Laborde) I found that the radium is setting off heat continually and in a very large amount, each gram of the radium is setting off in each hour 100 small calories, or in other words, it is setting off heat enough to melt in each hour its own weight in ice.''

'' Where is the source of energy ? Both M. Curie and myself are not able to go beyond some hypothesis.''

On page 20 there is this sentence : '' Prof. Curie took this ring which I have on my hand, which contains a small diamond, into his dark room and holding near it a small pill box containing about a gram of radium, caused the stone to phosphoresce most beautifully.''

Selenium is taken up on account of the change in its electrical resistance that is brought about by exposing it to light. Bell's radiophone, Duddell's talking arcs, and Ruhmer's wireless telephone are described under selenium. Finally, the work of Finsen on the treatment of disease by ultra-violet rays is discussed. Here, again, the author's self-consciousness shows itself as in the passage : '' The little cut of Prof. Finsen which heads this article is from an autograph portrait which Prof. Finsen presented to the writer.''   I. R.

A TEXT-BOOK OF ORGANIC CHEMISTRY. By WILLIAM A. NOYES, Professor of Chemistry in the Rose Polytechnic Institute. New York : Henry Holt & Co. 1903. pp. 524.

This book is intended for beginners. The author advises the student " to *read* all of the book as well as thoroughly to master, by careful study, some portions of it." He says : " The attentive reader will, by this means, gradually absorb many ideas by a process which is closely akin to the acquisition of a language by a child."

To quote further from the preface :   " The most radical departure from the method of treatment adopted in other books treating of the same subject consists in the dropping of the division into ' fatty ' and ' aromatic ' compounds and in the adoption of what appears to the author a more fundamental and logical classification. This novelty of arrangement will, it is hoped, be found to be justified partly by the fact that so many connecting links are now known between the two classes of bodies that they no longer stand isolated from each other ; and further it is believed that the new method of treatment brings out the important contrasts in chemical conduct for the two series fully as well as the old."

The further classification is described briefly by the author in the introduction :   " The hydrocarbons are considered first, as heretofore, and all classes of them together. Then follow oxygen compounds and compounds containing halogens, nitrogen, and sulphur, and finally, three chapters upon heterocyclic compounds, alkaloids, and compounds of physiological and pathological interest."

The book is undoubtedly scholarly. The author understands his subject and has a wide knowledge of it. He is, further, extremely painstaking and accurate, and he writes clearly. His judgment in the selection of his material is worthy of praise, and the arrangement of the material is logical—severely so. In short, in the opinion of the writer, the book is a good one, but he ventures to doubt whether the severely logical method adopted by the author is the best for beginners. Chapter VII. (pages 93–113) gives a very good account of the benzene series, including a clear and fairly full discussion of the structure of the fundamental hydrocarbon of the group. Succinylo-succinic ester and dihydroxyterephthalic ester, Ladenburg's prism formula, the Kekulé formula, the Claus formula, the thermochemical results of Brühl and of Thomsen are presented, and then, referring to the formulas, the author says : " The choice among these formulæ and their interpretation must be considered at present as uncertain. The proper attitude for a beginner, at least, is to

look upon the question as still an open one, and gradually to gather in his mind evidence as to one view or another till enough has been accumulated for an independent judgment.''

" So far as the practical investigation of aromatic compounds is concerned, the questions last discussed have little interest. In the study of these compounds the cyclic unions are the only ones which require consideration for almost all cases.''

Chapter VIII. (pages 114–120), presents the most complex hydrocarbons, including, of course, naphthalene, anthracene, and phenanthrene. Triphenylmethane and triphenylmethyl appear here also. In regard to triphenylmethyl the student is told that " It is the only hydrocarbon known which contains an odd number of carbon atoms.'' Of course, the author means " hydrogen atoms'' instead of " carbon atoms.''

Alcohols and phenols are taken up together in Chapter X (pages 124–163). The chapter begins with a helpful and perfectly correct list of all sorts and conditions of alcohols and phenols and their structural formulas. That list will strike terror into the breasts of beginners, and other tables of the same kind will be likely to produce the same result. There are two ways of teaching a subject. One is to make it easy at first and " hard'' afterward as the beginner gets strength. The other is to make it " hard'' at first, in the hope that it will become easy as the student goes on. It is, in general terms, the latter method that Professor Noyes adopts. Perhaps he is right. Who is to decide ? The writer of this notice confesses to a leaning, perhaps too great a leaning, to the other methods.

" Triazoacetic acid'' is given on page 463, although Hantzsch and Silberrad have shown that the acid to which Curtius gave this name on the supposition that it has the formula $(CHN_2.COOH)_3$, in reality has the formula $(CHN_2.COOH)_2$.   I. R.

DESCRIPTIVE CHEMISTRY. By LYMAN C. NEWELL, PH.D. (Johns Hopkins), Instructor in Chemistry, State Normal School, Lowell, Mass. Boston : D. C. Heath & Co. 1903. pp. 590.

The title of this text-book accurately describes its contents. The treatment of the subject is essentially descriptive, and the author states that the volume is prepared " for teachers who wish to emphasize the facts, laws, theories, and applications of chemistry.''

The text-book is divided into two parts, the first of which contains the descriptive text, together with the exercises and problems, and the second contains the experiments. The

text is divided into 31 chapters, the order in which the topics are presented being essentially that which is usually adopted. The discussion of law and theory follows the chapters treating successively of physical and chemical change, oxygen, hydrogen, water, and nitrogen and the atmosphere, while Gay-Lussac's law, Avogadro's hypothesis, and vapor-density follow the chapters on chlorine and hydrochloric acid, ammonia, and the oxygen compounds of nitrogen. The chapter treating of phosphorus, arsenic, antimony, and bismuth connects the non-metals with the metals, and the closing chapters of the text treat of the periodic law and spectrum analysis, and a description of representative members of the important classes of organic compounds. Each chapter is followed by a series of questions which serve at once as a means of review for the student and a valuable incentive—under encouragement from the teacher—to further reading. Stoichiometrical problems also accompany each chapter. An appendix contains data concerning the metric system, thermometry, crystallography, brief notes of chemical history and biography, atomic weights, and a list of reference books and supplementary reading. An admirable feature of the book is the introduction of the protraits of eminent chemists, which are distributed through the text.

The experiments of Part II. '' have been prepared to meet the needs of those schools in which the laboratory facilities are limited or the time for chemistry is short.'' The experiments appear to be carefully and happily selected although one can hardly escape the notion that the omission of the carefully prepared quantitative experiments which characterize his '' Experimental Chemistry'' has cost the author at least a sigh of protest and regret. From the present volume and the '' Experimental Chemistry'' taken together, it is surely possible to make a selection of quantitative or qualitative experiments which will be in accord with the most varied opinions. For those who prefer the experiments of the earlier volume as they stand, Part I. of this text-book is bound separately.

In these days of overcrowded curricula, overcrowded school rooms, and overtaxed energies, it is increasingly essential that the chemical instruction in our schools should be of such a character that it will broaden the pupil's horizon, hold his interest, and be within his grasp, and also of such a character that the instructor may hope to attain positive results with a minimum of attention to the individual, in many cases. Such a course can readily be selected from the experiments so care-

fully laid down in Dr. Newell's two books, and, whatever the nature of the course chosen may be, the text of the present volume must become an efficient aid. The statements are simple, direct, and clear, although the statement regarding chemistry (page 1), possibly because of its prominence, seems to suggest the criticism that it is less fortunately expressed than most others, and less so than the corresponding statement (page 15) of the author's earlier work. Unusual pains have been taken to eliminate errors of statement and to secure accuracy in proof-reading.

In the general treatment of the subject there is not much that is unique in this text-book ; the features which chiefly characterize it are its carefully considered statements, and the suggestive aids to study to be found in the questions, problems, and material in the appendix, all of which are plainly the outcome of earnest and thoughtful teaching. The book cannot fail to be of value to its readers—both teachers and pupils—whatever small differences of opinion there may be regarding the choice of some particular experiment, or form of phraseology.

It may fairly be regarded as a noteworthy addition to the host of text-books for school use, and if the teachers who make use of the manual will catch the spirit in which the volume has been written it will help to promote the adoption of rational courses in chemistry in secondary schools, which will be serviceable alike for those who expect to pursue the subject later in college, and for those whose chemical horizon must be bounded by the confines of their school instruction.

H. P. T.

AMERICAN

CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Harvard College.

ON CERTAIN ADDITION-COMPOUNDS DERIVED FROM ORTHOBENZOQUINONE.[1]

BY C. LORING JACKSON AND HORACE C. PORTER.

The work described in this paper was suggested by the discovery[2] of the aniline, ethyl alcohol, and methyl alcohol addition-compounds from dianilinodibromorthobenzoquinone, for it seemed probable that tetrabromorthobenzoquinone would also show a tendency to form addition-compounds, especially as the formation of such compounds from other ortho-quinones had been observed previously by Zincke and Arnst,[3] Zincke and Neumann,[4] and Zincke and Schaum[5] with alcohols or water, by Japp[6] with ketones, and by Klinger[7] with acetaldehyde. Zincke,[8] too, in his work on tetrabromortho-benzoquinone had noticed that glacial acetic acid, or a mixture of ether and ligroin, gave a white compound with it, and

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Horace C. Porter.

[2] This JOURNAL, **30**, 518 (1903).

[3] Ann. Chem. (Liebig), **267**, 319 (1892).

[4] *Ibid.*, **278**, 173 (1894).

[5] Ber. d. chem. Ges., **27**, 537 (1894).

[6] *Ibid.*, **17**, 2826 (1884) ; J. Chem. Soc. (London), **75**, 1034 (1899).

[7] Ann. Chem. (Liebig), **249**, 138 (1888).

[8] Ber. d. chem. Ges., **20**, 1776 (1887).

Koch and one of us[1] had prepared the puzzling white acetic acid product, but had made little progress toward settling its nature.

Our first experiments in this direction showed that the tetrabromorthobenzoquinone has a very strong tendency to combine with substances belonging to various classes and we selected for especial study at first its compounds with alcohols and with water. These bodies were obtained by allowing the solid tetrabromorthoquinone to stand with the substance at ordinary temperatures for some days or weeks (in the case of water moist toluol or benzol was used). The products are composed of 2 molecules of tetrabromorthobenzoquinone combined with one of the other substance. They are all white, crystallize in needles or prisms, and, although stable at ordinary temperatures and on crystallization from many solvents, are decomposed by heat, yielding as the principal decomposition-product the red hexabromorthoquinopyrocatechin ether, $C_6Br_4=O_2=C_6Br_2O_2$. This reaction in most cases runs quantitatively, thus :

$$(C_6Br_4O_2)_2CH_3OH \ = \ C_6Br_4O_2C_6Br_2O_2 + CH_3OH + Br_2.$$
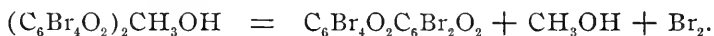
This strong similarity in properties has led us to class them together, and to call them α-compounds. We have prepared the following members of this series :

<div align="center">

α-Series.

Compound.	Melting-point.
$(C_6Br_4O_2)_2.H_2O$	$190°-200°$
$(C_6Br_4O_2)_2CH_3OH$ ·	$175°-185°$
$(C_6Br_4O_2)_2C_7H_7OH$	$165°-170°$
$(C_6Br_4O_2)_2CH_3COOH$	$220°-230°$

</div>

The so-called melting-points are really decomposition-points, as the substances are entirely converted into the red pyrocatechin ether at these temperatures ; consequently these points are much affected by the length of heating and other conditions, so that it is not worth while to try to fix them more definitely.

From the α-compounds a second series of isomeric bodies

[1] This JOURNAL, **26**, 42 (1901).

was obtained—the methyl compound by boiling the α-body with methyl alcohol, while the water and benzyl alcohol bodies, which could not be formed in this way, were made by the regulated action of acetic anhydride and dry sodic acetate on the α-compounds. All the compounds of the second series, which we designate with β, form white polygonal plates, melt at definite points without decomposition, and are remarkably stable toward heat, solvents, and many reagents. The following substances have been prepared :

β-Series.

Compound.	Melting-point.
$(C_5Br_4O_2)_2CH_3OH$	$261°$
$(C_6Br_4O_2)_2C_7H_7OH$	$216°$
$(C_6Br_4O_2)_2H_2O$	$222°$

The water substance was not analyzed, and is classed here only on the strength of its properties and mode of formation. The white acetic acid compound of Koch and one of us[1] seems to be related to these substances, although not belonging strictly in this series.

All these bodies, of whichever series, are much more stable than the compounds[2] previously discovered by us,

$$C_6Br_2(C_6H_5NH)_2O_2CH_3OH,$$
$$C_6Br_2(C_6H_5NH)_2O_2C_2H_5OH,$$
and $\quad C_6Br_2(C_6H_5NH)_2O_2C_6H_5NH_2,$
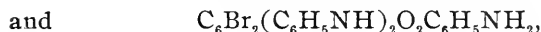
which evidently belong to a third series of addition-compounds, and are probably hemiacetals.

The three classes of addition-compounds just described do not include all those which can be formed from orthobenzoquinones, as two other different methods of addition have been observed by us already. The first product of the action of methyl alcohol on tetrabromorthobenzoquinone is a red com pound melting at 192° to 193°, and giving results, on analysis, agreeing with $(C_6Br_4O_2)_3CH_3OH$, but much more work is needed before even the formula of this body can be considered established. Further, toluol and acetophenone combine with tetra-

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[1] This JOURNAL, **26**, 42 (1901).
[2] *Ibid.*, **30**, 527 (1903).

bromorthobenzoquinone, giving red substances, $C_6Br_4O_2C_7H_8$ and $C_6Br_4O_2C_6H_5COCH_3$, which behave as if they were the quinone with toluol or acetophenone of crystallization, as they lose the volatile constituent by mere exposure to the air, leaving the tetrabromorthoquinone.

In working out the constitution of the α-addition-compounds, $(C_6Br_4O_2)_2ROH$, the most important point is to determine the way in which the two benzol rings are united. The union of carbon with carbon need not be considered, whether it is that of two atoms in the two benzol rings to form a diphenyl compound, or one in which the carbon of the added compound takes part, since a substance formed in this way would be too stable to fall easily into the hexabromortho-quinopyrocatechin ether, and this is the most striking property of the α-compounds. The union of the two quinone molecules must therefore take place through the atoms of oxygen, either by means of the quinone oxygen alone or the added substance may form a link in the connecting chain. In the latter case the most probable formula for the benzyl alcohol compound, for instance, would be this,
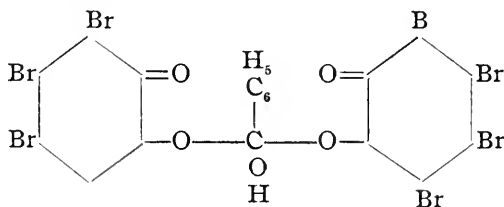
but this must be rejected for three reasons. (1) The water compound in this case would be entirely different from the alcohol compounds, whereas in fact they show the strongest similarity. (2) No satisfactory formula for the β-compounds can be worked out from this. (3) On decomposition with sulphuric acid this substance should give benzoic acid, or with hydrobromic acid, the tribromide, $C_6H_5CBr_3$, which would be easily converted into benzoic acid, but no trace of benzoic acid could be detected in the products from these reactions. The union of quinone atoms of oxygen with the oxygen of the added compound giving a chain of 3 atoms of oxygen is

so improbable, and would give such an unstable product, that it may be rejected without discussion.

The foregoing considerations leave only two possible formulas for these bodies :
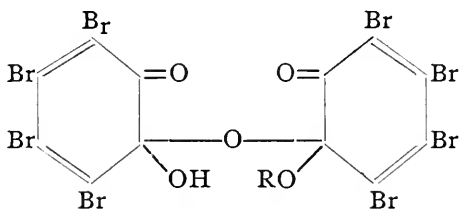
Formula I.
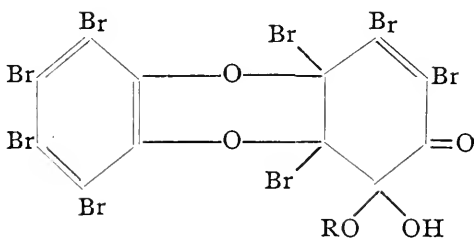
Formula II.

When this paper was written we thought that the analyses of the reduction-product and acet-reduction-product of the α-benzyl alcohol compound proved that Formula I. was correct. Subsequent work in this laboratory has thrown doubt on our interpretation of these analytical results, and therefore the determination of the true formula of the α-compounds must be postponed until a later paper. We have retained provisionally in the body of this paper the names of the compounds according to Formula I. so as to have names under which they can be indexed.

The properties and behavior of these bodies, as observed by us, are in harmony with both of these formulas. The white color is explained by the fact that the substances are no longer quinones, but oxides, corresponding to hemiacetals, and hemiacetals are usually colorless. The easy decomposition by heat into hexabromorthoquinopyrocatechin ether, bromine, and the alcohol (or water) would take place

as follows, if Formula I. is correct: The substance is first decomposed into 2 molecules of the tetrabromorthoquinone and the added compound, then the further action of the heat converts the orthoquinone into the pyrocatechin ether with evolution of bromine. That this is the effect of heat on tetrabromorthobenzoquinone was shown by a special experiment, in which it was heated to 130° to 150°, and in this way changed into hexabromorthoquinopyrocatechin ether with evolution of bromine. The reaction, however, did not run so smoothly as the similar decomposition of the α-bodies, since some other non-volatile product beside the pyrocatechin ether was formed. This difference can be easily explained by the part which the alcohol or water of the addition-compound would take in the reaction, since it would undoubtedly reduce some of the tetrabromorthoquinone to tetrabrompyrocatechin, which would make the formation of the ether neater and more complete.

When heated with hydrobromic acid the benzyl alcohol compound gives bromine, benzal, and possibly benzyl bromide and tetrabrompyrocatechin. Here the α-body has evidently split into benzyl alcohol or bromide and a quinone, which then oxidizes part of the hydrobromic acid, the free bromine converting the original benzyl bromide, in part at least, into benzal bromide. Hydrochloric acid acts in a similar way, but the action is complicated by the substitution of bromine by the free chlorine. With the methyl alcohol compound hydrochloric acid gave chloroform, but, as there was much free chlorine present, this is of no value in determining the constitution.

Sulphuric acid of sp. gr. 1.38 gave, with the benzyl alcohol compound as the principal product, the red hexabromorthoquinopyrocatechin ether, which, if Formula I. is correct, was undoubtedly formed by the action of 2 molecules of tetrabromorthoquinone on each other, after they had been set free by the action of the acid. The conversion of the α-bodies by aniline in hot benzol into the dianilinobromparaquinoneanil can be explained in the same way.

The solubility of all these compounds in sodic hydrate would

naturally follow from the presence of a hydroxyl group in the molecule. Finally, the formation of the β- from the α-bodies can be explained by a series of natural reactions, which, however, it is not worth while to discuss until the structure of the α-bodies has been settled.

The β-methyl alcohol compound is made from the α-body by warming it with methyl alcohol ; the β-benzyl alcohol or water compound is made by the regulated action of acetic anhydride on the corresponding α-substance.[1] They are so stable that they resist the action of most reagents. Almost the only positive observation made with them is that the methyl alcohol body contains a hydroxyl group, as it gives a monoacetyl derivative.

The white compound obtained by Koch and one of us[2] by evaporating glacial acetic acid over tetrabromorthoquinone is apparently related to the β-series, because it is formed from the α-body, first described in this paper, by heating it with acetic acid after the analogy of the methyl alcohol compounds, and also because of its unusual stability.

Tetrabromorthobenzoquinone gave white, or nearly white, compounds with substances belonging to the most various classes, but, since our work with toluol and benzol has shown that it has a remarkable attraction for water, we prefer to postpone all account of these experiments until they have been repeated with scrupulously dried materials.

<div align="center">EXPERIMENTAL PART.</div>

Action of Methyl Alcohol on Tetrabromorthobenzoquinone.

The tetrabromorthobenzoquinone $(C_6Br_4O_2)$ used in this work was prepared by the method of Zincke[3] with the slight modifications described in previous papers from this laboratory.[4]

The action of methyl alcohol on tetrabromorthoquinone gives rise to three compounds. Ten grams of tetrabromortho-

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[1] Sodium amalgam also converted the a-benzyl alcohol body partially into the β-. We are unable to explain this reaction.

[2] This JOURNAL, **26**, 42 (1901).

[3] Ber. d. chem. Ges., **20**, 1777 (1887).

[4] This JOURNAL , **26**, 34 (1901) ; *Ibid.*, **30**, 522 (1903).

quinone were mixed with 10 to 15 cc. of methyl alcohol and allowed to stand at ordinary temperatures in a corked flask. After twenty-four hours the quinone had completely dissolved, and a red crystalline solid had been deposited in considerable quantity, which was filtered out and purified for analysis. The mother-liquors contained hydrobromic acid, as was shown by testing them with argentic nitrate, but the amount was so small, 0.3 gram from 10 grams of the tetrabromorthoquinone, that it was obviously due to some secondary reaction.

The second product was obtained by allowing the red compound to stand for a longer time in contact with its mother-liquor. After four or five days it began to change into a cream-colored, crystalline body, and after two weeks this change was almost complete. This same cream-colored substance was obtained by the action of fresh methyl alcohol on the red compound, or by allowing the mother-liquors from the red body to evaporate in an open vessel. It is not further changed by the action of methyl alcohol in the cold, even when continued for ten weeks.

The third product was obtained by boiling for a few minutes the cream-colored substance with methyl alcohol, or a mixture of equal parts of methyl alcohol and benzol, when, on cooling, it separated in pure white crystals.

Red Addition-compound of Tetrabromorthobenzoquinone and Methyl Alcohol.—This substance, the product of the brief action of methyl alcohol in the cold on tetrabromorthoquinone, was purified by recrystallization from hot benzol and ligroin (3 : 2), dried at 60° to 70°, and analyzed with the following results :

I. 0.2972 gram substance gave, on combustion, 0.1904 gram CO_2 and 0.0177 gram H_2O.

II. 0.2697 gram substance gave, by the Carius method, 0.4680 gram AgBr.

III. 0.2444 gram substance gave 0.4244 gram AgBr.

	Calculated for $(C_6Br_4O_2)_3CH_3OH.$	I.	Found. II.	III.
C	17.48	17.48	....	....
H	0.31	0.66	....	....
Br	73.65	....	73.83	73.90

These analyses, however, are not sufficient to establish the formula, as $(C_6Br_4O_2)_4CH_3OH$ contains the following percentages: C 17.36, H 0.23, Br 74.08, so that it is obvious that analyses cannot decide on the true formula. The experiments tried by us so far have not thrown any light on the nature of this substance, but we hope some work now in progress in this laboratory may lead to the desired result. The yield was good, as 10 grams of the tetrabromorthoquinone gave 8.5 grams of the red substance.

Properties of the Red Compound.—It crystallized from a hot mixture of benzol and ligroin in small, transparent, well-formed prisms of a cherry-red color. It melts sharply at 192° to 193°, apparently without decomposition, and seems to be entirely stable at all temperatures below its melting-point. It is soluble in alcohol or benzol. Hot dilute sodic hydrate converts it into a white, crystalline body, and the solution turns yellow. This color is discharged by the addition of an acid.

The α-Addition-compound of Methyl Alcohol and Tetrabromorthoquinone (Tetrabromorthobenzoquinonemethylhemiacetal Oxide), $(C_6Br_4O_2)_2CH_3OH$.—This substance is the cream-colored product of the prolonged action of methyl alcohol on tetrabromorthoquinone in the cold. It was purified by two crystallizations from warm benzol (boiling benzol might produce a partial decomposition), dried *in vacuo*, and analyzed with the following result:

0.1478 gram substance gave, by the Carius method, 0.2516 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2CH_3OH$.	Found.
Br	72.73	72.44

The result of this analysis is confirmed by our analytical work on the benzyl alcohol compound, which corresponds to this in every respect, so that there can be no doubt about the correct formula of the substance. Hydrobromic acid was found in the mother-liquors, if the substance was made by the action of methyl alcohol on tetrabromorthoquinone, but none

was detected when it was made by adding fresh methyl alcohol to the red substance just described.

Properties of the α-Addition-compound with Methyl Alcohol.—
It crystallizes from warm benzol in short needles of a cream-white color. It is a substance of but slight stability as, although permanent in the cold, it begins to decompose slowly at temperatures as low as 50°, forming a red product. If dipped into a heated bath it melts at 178° to 182°, or rather decomposes to a brilliant red liquid, and this, like most other decomposition-points, is altered many degrees by changing the conditions of the heating. This decomposition is accompanied by an evolution of bromine, recognized by the color and smell of the vapor and its action with potassic iodide and starch. The red substance left behind showed the properties of the hexabrom-orthoquinopyrocatechin ether, $C_6Br_4O_2C_6Br_2O_2$, as it was insoluble in hot alcohol, did not melt below 300°, and crystallized from hot nitrobenzol in the flat, truncated needles characteristic of this body. The loss on heating was determined as follows :

0.1288 gram substance lost, on heating from 190° to 200° for twelve hours, 0.0261 gram.

	Calculated for $(C_6Br_4O_2)_2CH_3OH.$	Found.
Br_2+CH_3OH	21.82	20.26

This agrees with the results of the qualitative experiments and shows that the hexabromorthoquinopyrocatechin ether was formed with the loss of a molecule of bromine and one of methyl alcohol.

The substance is freely soluble in benzol or chloroform ; slightly soluble in alcohol or ligroin. Hot strong hydrochloric acid decomposes it in a manner described in the section on the constitution of these bodies ; dilute sodic hydrate dissolves it, and it is attacked by aniline in a hot benzol solution.

The β-Addition-compound of Methyl Alcohol and Tetrabrom-orthobenzoquinone, $(C_6Br_4O_2)_2CH_3OH.$—This substance was obtained by boiling the α-compound with methyl alcohol for a few minutes. The crystalline product was purified by one

crystallization from a mixture of equal parts of benzol and methyl alcohol, when it showed the constant melting-point 261°, and was dried at 100°, and analyzed with the following results :

I. 0.5152 gram substance gave, on combustion, 0.3377 gram CO_2 and 0.0254 gram H_2O.

II. 0.2569 gram substance gave 0.1713 gram CO_2 and 0.0157 gram H_2O.

III. 0.2158 gram substance gave, by the Carius method, 0.3697 gram AgBr.

IV. 0.1957 gram substance gave 0.3342 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2CH_3OH$.	I.	II.	III.	IV.
C	17.73	17.87	18.18	....	....
H	0.46	0.55	0.68	....	....
Br	72.72	....	....	72.91	72.67

A molecular weight determination by the boiling-point method in benzol gave the following result :

0.6245 gram substance in 15 grams of benzol gave a depression $\varDelta = 0°.123$.

	Calculated for $(C_6Br_4O_2)_2CH_3OH$.	Found.
Mol. wt.	880	883

Properties of the β-Methyl Alcohol Addition-compound.—It crystallizes from a mixture of benzol and methyl alcohol in white, rhombic plates, and melts at 261° apparently without decomposition. It is soluble in benzol or chloroform ; less soluble in ethyl or methyl alcohol or ligroin. Strong hydrochloric acid has no effect on it even after long heating to 150° in a sealed tube, but chars it at 200°. Strong sulphuric acid dissolves it slowly, forming a colorless solution. On the other hand, long boiling with sulphuric acid of sp. gr. 1.38 produces no effect. Strong nitric acid does not act on it, but fuming nitric acid produces a greenish color. Sodic hydrate is without effect on it, and the same is true of boiling hydriodic acid of a strength of 50 per cent, and of aniline in boiling benzol solution. In fact we have not yet found any reagent that is likely to give decomposition-products which will throw light on its nature.

The most striking property of this substance is its great stability, since it is not decomposed by heat even at its melting-point, and resists the action of most reagents at high temperatures. In this respect it forms a marked contrast to the α-compound, which begins to decompose at 50°.

Monoacetate of the β-Methyl Alcohol Tetrabromorthobenzoquinone, $(C_6Br_4O_2)_2CH_3OCOCH_3$.—One and a half grams of the β-compound described above were mixed with 8 grams of acetic anhydride and 2 grams of fused sodic acetate, and the mixture heated in a flask with a return-condenser to about the boiling-point of the acetic anhydride (130° to 140°) for eight hours. A large quantity of warm water was then added and the whole shaken until all the acetic anhydride had been removed. The dark residue, which looked as if it had been charred, was filtered out, washed, and recrystallized from a mixture of benzol and methyl alcohol, in which most of the blackened material was insoluble, until it showed the constant melting-point 249°, when it was dried at 100° and analyzed with the following result :

I. 0.1350 gram substance gave, by the Carius method, 0.2224 gram AgBr.

II. 0.1795 gram substance gave 0.2926 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2CH_3OCOCH_3$.	I.	II.
			Found.
Br	69.42	70.12	69.37

Properties of the Acetate.—It crystallizes from a mixture of benzol and methyl alcohol in bunches of needles, which, when more developed, appear as prisms terminated by a single plane at an acute angle. It melts at 249° without apparent decomposition, and in solubilities resembles the mother-substance.

Action of Benzyl Alcohol on Tetrabromorthobenzoquinone.

Ten grams of tetrabromorthobenzoquinone were mixed thoroughly with 8 to 10 cc. of benzyl alcohol and allowed to stand at ordinary temperatures in a corked flask. After two hours the red color of the quinone had faded to pink, and after twenty-four hours the mixture had become a viscous, pinkish-white mass. This was treated with a cold mixture of ether

and ligroin (2 : 1) repeatedly, until the thick benzyl alcohol mother-liquor had been removed, leaving a granular white residue, which was purified for analysis by recrystallization from a hot mixture of ether and ligroin (5 : 1), or benzol and ligroin (3 : 1). The former solvent proved the more effective, although the latter gave better crystals. A mixture of chloroform and ligroin, although it seemed admirably adapted for this purification, should not be used, as the product from this crystallization gave, on analysis, percentages of bromine 1 or 2 per cent above the true value, possibly from imprisoned chloroform. As the melting-, or rather, decomposition-point of the substance is indefinite, this effect of the chloroform could be detected only by analysis. The substance was washed with ligroin and dried *in vacuo* for analysis. Of the following analyses, I. and II. were purified with ether and ligroin in the manner described, III. with benzol and ligroin, the solution being boiled for two hours, IV. with hot benzol and ligroin, while V. is a sample that was only washed with the mixture of ether and ligroin but not recrystallized.

I. 0.2502 gram substance gave, on combustion, 0.2160 gram CO_2 and 0.0240 gram H_2O.

II. 0.2517 gram substance gave, by the Carius method, 0.3954 gram AgBr.

III. 0.1546 gram substance gave 0.2430 gram AgBr.

IV. 0.2210 gram substance gave 0.3449 gram AgBr.

V. 0.1777 gram substance gave 0.2773 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2C_7H_7OH$	I.	II.	Found. III.	IV.	V.
C	23.85	23.56	....	....	....	....
H	0.84	1.07	....	....	....	....
Br	66.95	....	66.84	66.89	66.41	66.41

These analyses leave no doubt as to the composition of the substance, and the fact that it decomposes easily, when heated turning red, and at 165° to 170° melting to a red liquid, shows that it is closely related to the α-methyl compound described earlier. It is therefore the α-benzyl alcohol tetrabromorthobenzoquinone, or to name it according to Formula I., tetrabromorthobenzoquinonebenzylhemiacetal oxide.

Properties.—It crystallizes from a mixture of benzol and ligroin in colorless, flat prisms or broad needles. Its decomposition-point lies been 165° and 170°, when it is heated rapidly, where it melts to a brilliant red liquid. Even at temperatures as low as 120° a similar decomposition takes place slowly, shown by the appearance first of a pink and, finally, of a red color. Bromine is given off during this decomposition, which was recognized by its color, smell, and action on potassic iodide and starch paste. A quantitative experiment showed that this decomposition was exactly similar to that of the corresponding methyl compound.

0.2669 gram substance, when heated at 160° to 200° for five hours, lost 0.0772 gram.

	Calculated for $(C_6Br_4O_2)_2C_7H_7OH$.	Found.
$Br_2 + C_7H_7OH$	28.03	28.92

The substance therefore loses 1 molecule of bromine and one of benzyl alcohol. The residue was recognized as hexabromorthoquinopyrocatechin ether by its red color, its crystalline form, and its essential insolubility in all solvents except nitrobenzol.

The α-benzyl alcohol compound is soluble in benzol, ether, chloroform, glacial acetic acid, or boiling ethyl alcohol, giving colorless solutions ; slightly soluble in ligroin. Strong hydrochloric or hydrobromic acid decomposes it at 100°. Sulphuric acid of sp. gr. 1.38 also acts on it when boiling. Fuming nitric acid turns it a deep bluish-green, and slowly dissolves it, forming a green solution which is decolorized by a drop of water. Hot dilute sodic hydrate decomposes it, and aniline in hot benzol converts it into the dianilinobromparaquinoneanil, melting at 173°. It has no immediate oxidizing effect on a mixture of potassic iodide and starch acidified with hydrochloric acid. Many of these reactions are described more in detail later in this paper.

The mother-liquors obtained in preparing this α-body from benzyl alcohol and tetrabromorthoquinone contained hydrobromic acid, probably due to a secondary reaction. On heating them to 100°, or warming with ethyl alcohol, a brilliant

red body was precipitated, which seemed to be the hexabrom-orthoquinopyrocatechin ether. As the α-body can be boiled with ethyl alcohol without reddening, these mother-liquors must contain some other substance. It was also observed that the crude α-substance obtained by washing out these mother-liquors dissolved completely in benzol or ethyl alcohol, showing that it contained none of the insoluble hexa-bromorthoquinopyrocatechin ether already formed.

β-Benzylalcoholtetrabromorthobenzoquinone,
$(C_6Br_4O_2)_2C_7H_7OH$.—We did not succeed in preparing this substance by warming the α-body with benzyl alcohol according to the method which was so successful with the methyl compound, but we obtained it by treating the α-compound with acetic anhydride in the attempt to make an acetyl α-derivative. In carrying on this process the proper conditions must be observed carefully, as at high temperatures the β-compound is decomposed by acetic anhydride.

Two grams of the α-benzylalcoholtetrabromorthoquinone were mixed with 8 grams of acetic anhydride and 2 grams of fused sodic acetate, and the mixture heated at 60° to 70° until it became bright-red. It was then allowed to stand ten to fifteen minutes, when it was treated with an excess of cold water and the insoluble pink residue filtered out, dried at 40° to 50°, and purified by crystallization from a hot mixture of methyl alcohol and benzol, which left an undissolved residue of the hexabromorthoquinopyrocatechin ether, recognized by its red color and crystalline form. The crystallization of the soluble portion was continued until it showed the constant melting-point 216° to 217°, when it was dried at 100° and analyzed with the following results:

I. 0.1478 gram substance gave, by the Carius method, 0.2313 gram AgBr.

II. 0.1839 gram substance gave 0.2885 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2C_7H_7OH$.	Found. I.	II.
Br	66.95	66.60	66.77

The two analyses were made with different preparations. The stability of the substance shows that it belongs to the

same series as the α-methyl alcohol compound previously described.

Properties of the β-Benzylalcoholtetrabromorthoquinone.—It crystallizes in white, polygonal plates, which melt at 216° to 217° with no apparent decomposition. It is soluble in benzol or ether; slightly soluble in alcohol or ligroin. Neither dilute sodic hydrate nor aniline in hot benzol have any action on the substance, so that, like the β-methyl compound, it is remarkably stable, but it is not so stable as this substance, since it is decomposed by acetic anhydride, as described in in the following section. The formation of the β-compound by the action of sodium amalgam on the α-body is also described later.

Action of Acetic Anhydride on the β-Benzyl Alcohol Compound.

One gram of the β-compound was mixed with 6 grams of acetic anhydride and 1 gram of fused sodic acetate, and the mixture heated at 120° to 150° until all had dissolved, which usually took place in four to five hours. The dark-colored solution was then diluted with water and the gray crystalline precipitate recrystallized from a hot mixture of 3 parts of benzol with 1 part of methyl alcohol, until it showed the constant melting-point 208° to 209°, when the grayish-white crystals were washed with methyl alcohol, dried at 60° to 70°, and analyzed with the following result :

0.1190 gram substance gave, by the Carius method, 0.1547 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2C_7H_7OCOCH_3$.	$C_6Br_4O_2C_7H_7OCOCH_3$.	Found.
Br	64.13	55.75	55.34

This analysis indicates that the acetic anhydride has decomposed the molecule of the β-compound, but it would be obviously unwise to discuss the nature of this decomposition on the present insufficient experimental data. This promising line of work will be continued in this laboratory during the coming year.

Reduction of the α-Benzylalcoholtetrabromorthoquinone.

Action of Zinc and Acetic Acid.—The α-benzylalcohol-

tetrabromorthoquinone was submitted to the action of coarsely powdered zinc and 95 per cent acetic acid in a series of test-tubes, 0.7 gram of the substance and about 10 cc. of acid being used in each tube. The action was started by warming for a few minutes, after which it was allowed to run by itself. The liquid turned very dark on cooling, and after standing for a short time deposited brownish needles, if the reduction had run well, which was not always the case by any means. These were filtered out and washed thoroughly with dilute acetic acid and warm water to remove the zinc acetate, after which they were purified by recrystallization from hot benzol. The substance was dried first in the air and afterward *in vacuo* for analysis.

0.1525 gram substance gave, by the Carius method, 0.2415 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2H_4C_7H_7OH.$	Found.
Br	66.67	67.40

The percentages of bromine in the reduced and original substances are so near together (66.67 and 66.95) that the analysis could not distinguish between them. The object of this analysis was to show that the reduction had not been accompanied by a decomposition of the molecule or the removal of bromine.[1]

Properties of the Reduction-product.—It crystallizes from benzol in clusters of pale straw-colored needles. It melts at 273° to 274°, and is decidedly more stable than the mother-substance. Its alcoholic solution gives a gelatinous precipitate with plumbic acetate ; nitric acid oxidizes it to a bright-red substance, soluble in alcohol, and melting at 295° to 300°, the nature of which we did not have time to determine. It will be studied during the coming year. Dilute sodic hydrate converts it into a violet-colored substance, insoluble in water.

Action of Acetic Anhydride on the Reduction-product.

This work was undertaken to determine how many hy-

[1] Later work has shown that this substance has not the composition assigned to it above. The determination of its true formula must be left for further study.

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droxyl groups were contained in the reduced substance. The reduction-product melting at 273° to 274° was heated to 100° for a few minutes with acetic anhydride and a little dried sodic acetate; the solid dissolved at first, but later a white precipitate was thrown down. To make sure that the reaction was complete the mixture was allowed to stand several hours, and then treated with water, filtered out, thoroughly washed, and dried *in vacuo* for analysis.

0.1097 gram substance gave, by the Carius method, 0.1529 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2H_2(COCH_3)_2C_7H_7OCOCH_3$.	Found.
Br	58.93	59.29

The formula with two acetyl groups contains the following percentage of bromine :

$$(C_6Br_4O_2)_2H_3(COCH_3)C_7H_7OCOCH_3\text{—Br } 61.31.$$

There can be no doubt, therefore, that the reduction-product contains three hydroxyl groups.[1] The triacetate is a white substance melting at 275° to 280° and is decidedly stable for a body of this class.

Action of Sodium Amalgam.—Some of the α-benzylalcohol-tetrabromorthoquinone was suspended in water and exposed to the action of 3 per cent sodium amalgam in a flask filled with carbonic dioxide. After the action had been continued for five days the product was examined and found to melt at 170° to 180° to a red liquid. This decomposition-point is higher than that of the original α-body (165° to 170°), and, although little weight can be given to these decomposition-points, because they are so much influenced by the conditions of heating, we are inclined to think that in this case a new substance has been formed, as on recrystallizing the crude moist product from alcohol and ether the β-compound melting at 216° was obtained, and special experiments have shown that the α-compound is not converted into the β- by crystallization from a moist mixture of alcohol and ether, nor by

[2] Later work throws doubt on the correctness of this formula as well as on that of the reduction-product.   C. L. J.

long standing with a strong solution of sodic carbonate. The study of this reaction must also be postponed till next year.

Behavior of Tetrabromorthobenzoquinone with Other Alcohols.

We have tried the action of the following alcohols on tetrabromorthobenzoquinone : Ethyl alcohol, normal propyl alcohol, isopropyl alcohol, isoamyl alcohol, allyl alcohol. In every case the action was allowed to run at ordinary temperatures, and products were obtained which were evidently mixtures of a white and a red substance. It seemed, therefore, that these higher alcohols acted in two ways, first by forming addition-compounds similar to that from methyl alcohol, and, secondly, by reducing some of the tetrabromorthoquinone to tetrabrompyrocatechin, which then acted on unaltered quinone to form the red hexabromorthoquinopyrocatechin ether. Under these circumstances we have postponed the study of the products from these other alcohols until the work on the simpler reactions with methyl or benzyl alcohol was more nearly finished.

Behavior of Tetrabromorthobenzoquinone with Toluol.

Five grams of the tetrabromorthoquinone were dissolved in 5 cc. of cold ordinary toluol (which had been redistilled but not dried over sodium), and the solution allowed to stand at ordinary temperatures in a corked flask. After several hours, or sometimes in a few minutes, if the mixture was shaken, the solution became pasty from the separation of a red addition-compound of tetrabromorthoquinone and toluol. If these red crystals were allowed to stand longer with their mother-liquor, after about eight days it was found that a paler red crystalline deposit had formed, which proved to be a compound of tetrabromorthoquinone and water. The mother-liquor from these crystals contained hydrobromic acid, and, if heated, or treated with alcohol or ether, formed a brilliant red, insoluble body, identified by its crystalline form as the hexabromorthoquinopyrocatechin ether. The crystals, on the other hand, contained none of this substance, as they were completely soluble in alcohol.

Tetrabromorthobenzoquinone with Toluol of Crystallization, $C_6Br_4O_2C_7H_8$.—The preparation of this substance has been described in the preceding section. It was obtained from the solution of tetrabromorthoquinone in toluol, even when it was saturated with water, as was shown by an experiment from which we expected to get more of the water compound by this device.

As it was very efflorescent, it was prepared for analysis simply by pressing as rapidly as possible between filter-paper.

0.9368 gram substance lost, when exposed to the air, 0.1745 gram. *In vacuo* there was an additional loss of 0.0019 gram.

	Calculated for $C_6Br_4O_2C_7H_8$.	Found. Air.	Vacuum.
Toluol	17.83	18.59	18.82

The numbers are as near as could be expected, considering the difficulties in the way of preparing the substance for analysis. Practically all the toluol (0.1742 gram) escaped after the substance had been exposed to the air for twenty-four hours. The residue was tetrabromorthoquinone. A second sample of the crystals, dried between filter-paper as before, was analyzed.

0.4300 gram substance gave, by the Carius method, 0.6247 gram AgBr.

	Calculated for $C_6Br_4O_2C_7H_8$.	Found.
Br	62.01	61.81

Properties of Tetrabromorthoquinone with Toluol of Crystallization.—It forms transparent, garnet-red prisms or large rectangular plates. It melts at 70° to 75°. As this is really a solution of the quinone in the separated toluol, no sharper result could be expected. Upon heating the melting-tube more intensely, the toluol vapors distil off and can be burnt at the mouth of the tube. If heated in an open tube to 100° for some time, the dark-red melted substance gradually becomes lighter, and at last solidifies to a yellowish-white, crystalline mass; the vapors given off contain bromine as shown by potassic iodide and starch and by bleaching litmus, and have the odor and action on the eyes of benzylbromide. The yellowish-

white residue, when recrystallized from a mixture of chloroform and ligroin, gives yellow, tapering needles, softening at 226° without reddening. When boiled with alcohol it gives a brilliant red substance. We were obliged to postpone the investigation of this product till the coming winter.

α-Compound of Tetrabromorthoquinone and Water.—The preparation of this substance by the action of common toluol on tetrabromorthoquinone has been described already. Ordinary benzol gave the same product. Analysis V. was made with a sample prepared with benzol. The preparation of this substance from apparently dry toluol or benzol shows that the tetrabromorthoquinone has a remarkably strong attraction for water ; in fact, we did not succeed in getting our materials dry enough to avoid the formation of this water compound, but we prefer to postpone the description of our work in this direction until additional experiments have been tried.

The compound with water was purified by washing with a cold mixture of benzol and ligroin, which changed the color from light-red to yellowish-pink, and crystallizing from the same mixture hot. It was dried *in vacuo* and analyzed with the following results :

I. 0.2683 gram substance gave, on combustion, 0.1650 gram CO_2 and 0.0080 gram H_2O.

II. 0.2325 gram substance gave, by the Carius method, 0.4042 gram AgBr.

III. 0.2993 gram substance gave 0.5202 gram AgBr.

IV. 0.2565 gram substance gave 0.4447 gram AgBr.

V. 0.2709 gram substance gave 0.4724 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2 \cdot H_2O$.	I.	II.	Found. III.	IV.	V.
C	16.63	16.78	....	....	....	....
H	0.23	0.34	....	....	....	....
Br	73.91	....	73.99	73.98	73.78	74.21

In purifying the substance a mixture of chloroform and ligroin must not be used, although it gives excellent crystals, as the analyses of such samples for halogens gave varying results too high for the theory. That this compound belongs

to the α-series is shown by the fact that it decomposes, giving a red compound when heated.

Properties of the α-Water Compound.—It crystallizes from benzol in colorless, tapering, flat needles. Its decomposition-point lies between 190° and 200°, when it is dipped into the heated bath, as between those temperatures it melts to a brilliant red liquid. This same decomposition takes place slowly at temperatures of about 160°, as shown by the appearance of the red color. Bromine was one of the products of this reaction, proved by its color, odor, bleaching power, and a test with potassic iodide and starch. The decomposition was studied quantitatively, as follows :

0.2080 gram substance lost, when heated for three hours at 190° to 200°, 0.0434 gram.

	Calculated for $(C_6Br_4O_2)_2.H_2O$.	Found.
$Br_2 + H_2O$	20.55	20.87

The residue was identified as the hexabromorthoquinopyrocatechin ether by its color, crystalline form, and other properties.

The substance is soluble in benzol, chloroform, alcohol, ether, or glacial acetic acid ; very slightly soluble in ligroin. The three strong acids do not affect it in the cold, but hydrochloric acid (or hydrobromic acid) at 100°, and boiling sulphuric acid of sp. gr. 1.38, decompose it, as described in detail in a later section. Fuming nitric acid forms with it a pale greenish solution. Dilute sodic hydrate dissolves it easily, and the unaltered substance seems to be precipitated on acidification, but a strong solution of sodic hydrate does not dissolve it.

The β-Watertetrabromorthobenzoquinone, $(C_6Br_4O_2)_2.H_2O$.— This substance was made from the α-body by the regulated action of acetic anhydride in the way used for the preparation of the corresponding benzyl alcohol compound. Two grams of the α-substance were mixed with 8 grams of acetic anhydride and 2 grams of dried sodic acetate. The mixture turned bright-red almost immediately, and, after warming for a minute or two, was diluted with a large quantity of water

and the reddish precipitate filtered out. This was dried and treated with a mixture of 10 parts of methyl alcohol and one of benzol which dissolved most of it, but left a brilliant red residue. The solution, on evaporation, deposited a pure white, crystalline substance, which, after purification, showed the constant melting-point 221° to 222°. As it melts without decomposition, and crystallizes in polygonal plates like the other β-bodies, there can be little doubt that it is the β-watertetrabromorthoquinone. It is soluble in ether, benzol, or ligroin (difference from the α-body) ; slightly soluble in alcohol. Hot dilute sodic hydrate does not affect it, nor does aniline in a hot benzol solution.

The further action of acetic anhydride gave products with low melting-points, probably resulting from the splitting up of the molecule of the β-compound. Care must be taken, therefore, in preparing this substance that the action of the acetic anhydride does not run too far.

Certain Reactions of the Water and Alcohol Compounds.

This work was undertaken in the hope of settling the constitution of these substances and is described here, since it throws light on their properties, although it turned out of little value in the determination of their structure.

α-Compounds.

Action of Hydrochloric Acid.—One gram of the methyl alcohol compound, $(C_6Br_4O_2)_2CH_3OH$, heated with strong hydrochloric acid for thirty hours to 100° gave a deep-yellow liquid and long white needles. A drop of the acid liquor gave a deep-blue with potassic iodide and starch, and the vapors bleached moist litmus, showing the presence of chlorine or possibly bromine. On distilling with steam the first portions of the distillate were turbid, had a distinct chloroform odor, and gave the isonitrile test with aniline and sodic hydrate. The residue, after filtration, yielded on evaporation yellowish-white needles melting at 185° to 187°, giving a deep-green color with ferric chloride, and a precipitate with plumbic acetate in boiling aqueous solution. They are undoubtedly,

therefore, a pyrocatechin, and probably tetrabrompyrocatechin which melts according to Stenhouse at 187°, according to Zincke at 192° to 193°. The products identified were, therefore, chlorine (or bromine), chloroform, and a substituted pyrocatechin.

The benzyl alcohol compound, $(C_6Br_4O_2)_2C_7H_7OH$, gave with hydrochloric acid, under the same conditions, chlorine or bromine, either benzyl chloride or bromide, to judge by the smell, and a substituted pyrocatechin (proved by the usual reactions), which distilled with steam, and therefore was not tetrabrompyrocatechin, which cannot be distilled with steam. This was probably a chlorbrompyrocatechin, formed by the action of the chlorine on the tetrabrompyrocatechin, which must be the first product of the reaction. As this product seemed of but slight interest, it was not studied more thoroughly.

The water compound, treated with hydrochloric acid, gave bromine in considerable quantity.

Hydrobromic Acid.—When we studied the action of hydrochloric acid on the benzyl alcohol compound,

$$(C_6Br_4O_2)_2C_7H_7OH,$$
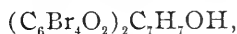
we found, as just stated, that the chlorine set free had a substituting action upon the tetrabrompyrocatechin. To remove this complication we took up the action with hydrobromic acid (redistilled, boiling-point 126°, containing 48 per cent of HBr). The substances were heated together in a sealed tube for thirty hours to 100° and the products were bromine, benzal bromide with perhaps benzyl bromide, and tetrabrompyrocatechin. The bromine was identified by its action with potassic iodide and starch paste. The benzal bromide was separated from the tetrabrompyrocatechin by distillation with steam, as the latter is not volatile under these conditions. The distillate contained 1 or 2 drops of oil with a strong odor like benzyl bromide. Upon heating about 5 cc. of the mixture of oil and water in a sealed tube to 125° for four hours the odor of benzaldehyde was very distinct, the irritating smell had vanished, and the aqueous liquid gave a test for

bromine with chlorine water. From this we infer that the oil was, in part at least, benzal bromide, but it is possible, in fact probable, that it also contained benzyl bromide, perhaps in considerable amount. The tetrabrompyrocatechin obtained as a residue from the distillation with steam was recognized by the melting-point 186° to 187° (Stenhouse found 187°, Zincke 192° to 193°), the dark green color with ferric chloride, the precipitate with plumbic acetate, and the formation of the red tetrabromorthoquinone with nitric acid. It seemed evident from these results that the acid breaks up the α-benzyl alcohol compound into tetrabromquinone and benzyl bromide. The quinone then sets free bromine from the hydrobromic acid, becoming itself tetrabrompyrocatechin, and the bromine converts the benzyl bromide wholly or in part into benzal bromide.

Action of Sulphuric Acid.—The α-benzyl alcohol compound, $(C_6Br_4O_2)_2C_7H_7OH$, was boiled in a flask with a return-condenser for three hours with sulphuric acid of sp. gr. 1.38. Oily drops were observed in the condenser, and there was a strong, irritating odor. The principal product, a yellowish-red solid, on treatment with alcohol, left a considerable amount of the red hexabromorthoquinopyrocatechin ether recognized by the usual properties and the following analysis :

0.2149 gram substance gave, by the Carius method, 0.3494 gram AgBr.

	Calculated for $C_6Br_4O_2C_6Br_2O_2$.	Found.
Br	69.77	69.19

Tetrabrompyrocatechin gave none of the ether on similar treatment with sulphuric acid. The filtrate from the ether contained bromine and hydrobromic acid, but this observation has not much significance, as it was found that the red ether, when boiled with a few drops of bromine and sulphuric acid, gave hydrobromic acid, and that tetrabromorthoquinone also formed hydrobromic acid when boiled with water for two hours.

The water compound, $(C_6Br_4O_2)_2.H_2O$, treated in the same way with sulphuric acid of sp. gr. 1.38, gave the red hexabromorthoquinopyrocatechin ether.

β-*Compounds.*

The methyl alcohol compound, $(C_6Br_4O_2)_2CH_3OH$, melting at 261°, was the only one studied. Hydrochloric acid had no action on it even at 140° to 160° for thirty hours, as was proved by recovering the amount of compound used entirely unaltered. After heating to 200° for forty-eight hours the substance was charred.

Hydriodic Acid.—The β-methyl alcohol compound was boiled with hydriodic acid (50 per cent HI) tor forty minutes in a flask with a return-condenser, but there was no action, as we recovered the whole of the substance unaltered.

Sulphuric acid, of sp. gr. 1.38, also had no action on the β-methyl alcohol compound after boiling for two hours. It is evident from these experiments that the β-methyl alcohol compound is a remarkably stable substance. Similar experiments with the β-benzyl alcohol compound will be tried in this laboratory, as it seems to be less stable than the methyl alcohol body.

Addition-compounds of Acetic Acid and Tetrabromorthobenzoquinone.

In the first paper of this series, W. Koch and one of us[1] described a white compound formed by the action of glacial acetic acid on tetrabromorthoquinone, but owing to its remarkable stability no formula could be assigned to it with certainty. We have made little progress on the continuation of this work, because we thought it wiser to study the more manageable alcohol compounds first, in order to gain experience which would help us to solve this difficult problem. All the work described in this section, therefore, must be considered preliminary experiments.

In preparing the substance by the method given in the paper already referred to we obtained by the repeated evaporation of glacial acetic acid in contact with tetrabromorthobenzoquinone on the steam-bath a yellowish-white residue, which, on treatment with hot alcohol, deposited a slight amount of a vermilion-red precipitate. This increased in

[1] This JOURNAL, **26**, 42 (1901).

quantity as the boiling with alcohol was continued, so that after fifteen to twenty minutes boiling the red insoluble substance seemed to form the only product of the reaction. The red product was identified by its properties as hexabromorthoquinopyrocatechin ether. It was also formed when the crude product was boiled with acetone, ethyl acetate, or water. That none of it existed in the crude product of the action of acetic acid on orthoquinone was shown by the fact that this dissolved completely in cold benzol. We must therefore correct the statement of Koch and one of us that the red insoluble compound was formed by the action of acetic acid on tetrabromorthoquinone. The small amount observed by them was formed by the subsequent treatment of the crude product with alcohol.

To obtain the white compound, the crude product was extracted as quickly as possible with hot alcohol, the extract allowed to stand for a time, filtered, and precipitated with water. This precipitate was warmed for some time with a little glacial acetic acid and then dissolved in boiling glacial acetic acid, filtered from the red insoluble portion, and crystallized from the boiling acid. It was dried by exposure to dry air at 40° to 50° and analyzed with the following result:

0.1761 gram substance gave, by the Carius method, 0.2865 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2CH_3OH$.	Found.
Br	70.48	69.26

These results leave much to be desired, but can hardly be brought into harmony with any other probable formula.

Properties.—It crystallizes from glacial acetic acid in large, yellowish-white, efflorescent, rectangular plates or prisms. It melts at 220° to 230° with decomposition, forming a red liquid. On being heated for several hours near its melting-point it gave up bromine, detected by its odor and the reaction with potassic iodide and starch, and left a brilliant red substance, which, however, did not seem to be the hexabromorthoquinopyrocatechin ether to judge by the form of its crystals. The loss in weight, too, did not agree with that calculated for

$CH_3COOH + Br_2$. The acetic acid compound is soluble in alcohol, benzol, ether, chloroform, or glacial acetic acid ; very slightly soluble in ligroin. Dilute sodic hydrate dissolves it easily with a dark color, indicating a decomposition of the substance. Aniline in hot benzol converts it into the dianilinobromparaquinone anil. All these properties show that the substance is not identical with the very stable white compound prepared by Koch and one of us.[1] That a compound such as this was formed at first is indicated in the paper referred to by the statement that the crude product was freely soluble in alcohol, but, as the crystallization from glacial acetic acid continued it became less and less so, until, when pure, it was nearly insoluble in alcohol. To judge from these preliminary experiments, the substance prepared by us corresponds to the α-addition-compounds of alcohols and tetrabromorthoquinone, and it seems probable that the more stable body is in some way related to the β-compounds.

Glacial acetic acid, if allowed to stand in the cold with tetrabromorthoquinone, gave two products, which seemed to be entirely different from any of those as yet studied by us. This work will be continued.

Action of Acetophenone on Tetrabromorthobenzoquinone.

This work was taken up in the hope that it would throw light on the action of acetic acid on the tetrabromorthoquinone. At first the action was carried on hot, as it was in this way that the acetic acid compound had been obtained. Later, after the work with alcohols, the action was carried on at ordinary temperatures with a different result.

Action at the Boiling-point.—Two grams of tetrabromorthoquinone were boiled in a flask with a return-condenser with 25 cc. of acetophenone. On standing over night the very dark-colored product deposited pale-yellow, long needles, which, after purification by washing with acetic acid and crystallization from a mixture of alcohol and chloroform, were recognized as triphenylbenzol by the melting-point, $171°$, and the following analysis :

[1] This JOURNAL, **26**, 42 (1901).

0.1392 gram substance gave, on combustion, 0.4773 gram CO_2 and 0.0725 gram H_2O.

	Calculated for $C_6H_3(C_6H_5)_3$.	Found.
C	94.12	93.53
H	5.88	5.78

It is evident that the tetrabromorthoquinone was decomposed under these circumstances with the formation of hydrobromic acid (detected in the crude product), which then converted the acetophenone into the symmetrical triphenylbenzol. All attempts to isolate the other products of the reaction failed. Nor were we more successful when the reaction was carried on at as low a temperature as 65°.

Action at Ordinary Temperatures. Tetrabromorthobenzoquinone with Acetophenone of Crystallization.—Five grams of the tetrabromorthoquinone were dissolved in 5 cc. of cold acetophenone, and the clear solution allowed to stand twenty-four hours, when it was found that well-formed, transparent, red prisms had been deposited. As they effloresced rapidly, they were prepared for analysis by pressing them quickly in filter-paper.

0.7064 gram substance lost, *in vacuo* in twenty days, 0.1567 gram, which increased by 0.0060 gram after twelve days more.

	Calculated for $C_6Br_4O_2C_6H_5COCH_3$.	Found. 20 days.	Found. 32 days.
$C_6H_5COCH_3$	22.06	22.19	23.04

The residue was tetrabromorthoquinone.

0.3103 gram substance gave, by the Carius method, 0.4234 gram AgBr.

	Calculated for $C_6Br_4O_2C_6H_5COCH_3$.	Found.
Br	58.82	58.03

These results are as good as could be expected, when the imperfect method of drying the substance is remembered.

It forms red prisms, which melt, or rather dissolve in the liberated acetophenone between 50° and 60°. In its solubilities it resembles tetrabromorthoquinone. On long standing with acetophenone it is converted into a yellow crystalline

substance, which resembles the α-addition-compounds in properties, but its analysis gave such perplexing results that we think it wiser to say no more about it until further experiment has made its nature clear.

The action of other reagents on tetrabromorthoquinone was also studied, but in view of the strong attraction it shows for water we prefer to postpone all account of these experiments until they have been repeated under more carefully regulated conditions. It is worth mention, however, that ligroin (boiling from 40° to 70°) gave with the tetrabromorthoquinone yellowish-red prisms, which were white when powdered. This is probably the white product obtained by Zincke[1] from the action of a mixture of ether and ligroin on tetrabromorthoquinone.

Certain Reactions of Tetrabromorthobenzoquinone.

These observations were made usually as parallel experiments in the course of our work on the addition-compounds, and may be collected here for convenience.

Decomposition by Heat.—About 1 gram of tetrabromorthoquinone was heated in an air-bath at 130° to 150°. Bromine was evolved, as shown by the odor and test with potassic iodide and starch. The residue, which was somewhat lighter red than the quinone, upon extraction with boiling alcohol was separated into a white soluble substance melting between 180° and 190°, and giving no test for a pyrocatechin with ferric chloride, and a red substance insoluble in the alcohol, which looked like hexabromorthoquinopyrocatechin ether. Upon crystallizing this body from nitrobenzol rather indefinite crystals were obtained instead of the flat truncated needles characteristic of the ether, and an analysis gave 68.48 per cent of bromine instead of 69.77. It is safe to assume that the presence of the impurity indicated by this analysis caused the difference in the crystalline form, and that the substance is really the pyrocatechin ether.

Decomposition by Boiling Water.—Two grams of the tetrabromorthoquinone were mixed with 50 cc. of water by thor-

[1] Ber. d. chem. Ges., **20**, 1778 (1887).

ough shaking, and then boiled for an hour in a flask with a return-condenser. The liquid faded from red to a pale straw-color, and, when filtered and evaporated, deposited a yellow-ish compound, giving only a faint test for a pyrocatechin with ferric chloride. It also contained hydrobromic acid. The insoluble residue, after extraction with boiling alcohol, con-sisted of hexabromorthoquinopyrocatechin ether.

Fuming nitric acid dissolved tetrabromorthoquinone to a clear purple-red, or claret-colored solution. Dilution with water precipitated the quinone unaltered. On heating the quinone with fuming nitric acid a pale yellowish solution was formed.

The study of these addition-compounds of tetrabromortho-benzoquinone will be continued in this laboratory, and its ac-tion with other reagents investigated. The attempt will be made also to prepare similar addition-compounds from other orthoquinones.

CAMBRIDGE, MASS., Aug. 22, 1903.

ACTION OF ALCOHOLS ON THE TETRAZONIUM CHLORIDES DERIVED FROM BENZIDINE AND FROM ORTHOTOLIDINE.[1]

BY J. H. C. WINSTON.

The investigation, the results of which are presented in this article, is a continuation of the larger investigation[2] on the action of alcohols on diazo compounds that has been car-ried on for a number of years past in this laboratory under the guidance of Professor Remsen. It deals especially with the action of methyl, ethyl, and propyl alcohols under different conditions on the tetrazonium chlorides obtained from benzi-dine hydrochloride and from orthotolidine hydrochloride.

Preparation of Metaditolyltetrazonium Chloride.—The toli-dine used was prepared from commercial *o*-tolidine. This

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[1] From the author's dissertation submitted, June, 1899, to the Board of University Studies of the Johns Hopkins University, in conformity with the requirements for the degree of Doctor of Philosophy. The investigation was undertaken at the sug-gestion of Professor Remsen and carried on under his guidance.

[2] For earlier investigations in this series see This JOURNAL, **4,** 374 ; **8,** 243 ; **9,** 387; **11,** 319 ; **15,** 124, 301, 320, 379 ; **16,** 235 ; **19,** 163, 563, 831 ; **20,** 229, 298, 458.

was purified by converting it into the hydrochloride, treating this in solution with bone-black, and precipitating the tolidine with potassium hydroxide.   It crystallizes from water in beautiful pearly leaves, melting at 126°.5.   In the preparation of the tetrazonium chloride it was found best to use freshly-made tolidine hydrochloride, precipitated in finely divided condition by addition of strong hydrochloric acid to a water solution of the hydrochloride.   To prepare the tetrazonium chloride, take tolidine hydrochloride and water in the proportion of 3 parts of water to 1 of the salt.   Add a part of the salt first and then pass nitrous fumes from arsenious oxide and nitric acid into the paste.   As this clears up, add more of the salt, and continue this until the action is complete and a clear, light straw-yellow solution is obtained.   Pour this into about three times its volume of 95 per cent alcohol, which has been previously cooled in a freezing-mixture of salt and ice.   The tetrazonium salt is at once precipitated in the form of a flocculent yellow substance.   This is then filtered off through a Büchner funnel, washed with alcohol and ether, and spread on drying-paper.   The yield is about 80 per cent of the theoretical.

Action of Absolute Methyl Alcohol upon Metaditolyltetrazonium Chloride.—The action was carried on in a flask connected with a return-condenser, the flask being placed on a water-bath. The decomposition began only when the temperature reached almost that of the boiling-point of the alcohol, and then proceeded smoothly with the copious evolution of nitrogen until the reaction was completed and a perfect solution resulted. This required half an hour.   The solution was then boiled for a few moments to insure complete decomposition.   During the whole operation no odor of aldehyde was perceptible.   As the decomposition proceeded the alcoholic solution changed color, gradually darkening, until at the end it was of a deep red color.   On allowing the solution to cool, crystals in the form of reddish leaves separated, which were removed by filtration. Upon evaporation of a large part of the alcoholic mother-liquor a very small crop of crystals was obtained.   The rest of the alcohol was then removed by distillation and was of a

slightly yellow color. This was poured into a beaker and 6 volumes of a saturated solution of sodium chloride added, but no oil separated. The color of the alcohol was probably due to particles of the tarry residue, mechanically carried over during the process of distillation. The tarry oil remaining in the distillation-flask was easily soluble in ordinary alcohol, but from this solution nothing of value was ever obtained. Purification was attempted by means of animal charcoal, but the reddish color could not be thereby removed. On partial evaporation nothing was obtained in crystalline form, and on complete evaporation of the alcohol the same unpromising oil resulted. Some of this was allowed to stand for weeks, in the hope that something would crystallize out. Solidification by means of a freezing-mixture was attempted, but it remained always the same tarry oil. Some of it was put in a distillation-flask and subjected to distillation. The residue remaining in the flask after the last traces of alcohol and water were removed solidified to a non-crystalline black cake, from which nothing definite could be obtained. It was thought that if any of the hydrocarbon corresponding to this tolidine, which is known to be an oil, was present it could be separated from the tar by distillation with water vapor, so to the flask containing the tar a little water was added, and then steam passed through the flask, but no oil was carried over with the water vapor. The crystals, which had been obtained by the action of methyl alcohol on tetrazo-*m*-ditolyl chloride, were dissolved in ordinary alcohol, the solution decolorized with animal charcoal, and from this, on allowing a hot concentrated solution to cool, the substance was obtained in the form of beautiful, almost colorless, leaves. These were recrystallized until the melting-point became constant, and were then obtained as silvery leaves having the sharp melting-point 145°.5. This substance is insoluble in water, very sparingly soluble in cold alcohol and ether, rather soluble in boiling alcohol. The difference in solubility in alcohol at its boiling temperature and a few degrees below, is very marked.

Two analyses gave the following results :

I. 0.2000 gram substance gave 0.5801 gram CO_2 and 0.1337 gram H_2O.

II. 0.2000 gram substance gave 0.5812 gram CO_2 and 0.1336 gram H_2O.

The calculated percentages of the elements for dimethoxy-*m*-ditolyl $(C_{14}H_{12}(OCH_3)_2)$ are :

	Calculated.	I.	II.
		Found.	
C	79.34	79.10	79.11
H	7.44	7.43	7.43
O	13.22	13.47	13.46

There are two ways in which the reaction between tetrazonium chloride and methyl alcohol might take place. The two reactions are represented in the following equations :

I. $C_{14}H_{12}N_4Cl_2 + 2CH_3OH =$
$$C_{14}H_{14} + 2CH_2O + 2N_2 + 2HCl ;$$
II. $C_{14}H_{12}N_4Cl_2 + 2CH_3OH = C_{14}H_{12}(OCH_3)_2 + 2N_2 + 2HCl.$
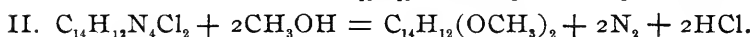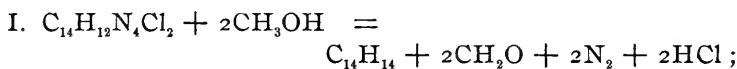
It is observed that in the case of the substances brought together in the decomposition described above and under the conditions indicated, the reaction takes place in accordance with the second equation, and, indeed, the most careful search failed to reveal any evidence that the first reaction takes place at all when this tetrazonium salt is treated with methyl alcohol under the given conditions. It was considered advisable to vary the conditions of the reaction to determine how the decomposition is best effected, and also to study the effects of variations in temperature and dilution of the alcohol, as well as the presence of certain substances known to affect the reaction, generally speaking.

Decomposition of the Tetrazonium Salt at Room Temperature. —About 15 grams of the diazo compound were placed in a half-liter flask and 250 cc. of absolute methyl alcohol added, and the mixture allowed to stand at room temperature for a fortnight, alcohol being added from time to time to make up for evaporation. By the end of this time most of the salt had gone into solution and the alcohol had turned dark-red, but at no time was an evolution of nitrogen noticeable, neither was the odor of aldehyde perceptible. The flask was now attached to a return-condenser and the alcohol boiled on a water-

bath, when nitrogen was evolved freely and the reaction was complete in half an hour. The yield of the crude ether was a little over 4 grams, but this was not as pure as that made in the decomposition of the freshly-prepared salt. All efforts to obtain the hydrocarbon from the alcohol distilled off and from the residue in the distillation-flasks were as futile as those described above.

Decomposition of the Tetrazonium Salt at the Boiling Temperature of Methyl Alcohol.—Fifteen grams of the same tetrazonium salt were decomposed with absolute methyl alcohol at the boiling temperature of the alcohol. The decomposition was complete in half an hour, the evolution of nitrogen being rapid and the solution reddening as before. About 4 grams of the ether were obtained, which substance was not as deeply colored as that obtained in the preceding experiment. As before, no other product was isolated, and it seems that only the '' methoxy'' reaction takes place in this decomposition. An attempt was next made to determine the effect of diluting the alcohol with water.

Decomposition of the Tetrazonium Salt with Dilute Methyl Alcohol.—Twenty-three grams of the salt were decomposed with methyl alcohol diluted with 5 per cent of its volume of water. The decomposition was accomplished in the usual manner by heating the mixture to the boiling-point of the alcohol, when the reaction proceeded smoothly and quickly. On cooling, 5 grams of dimethoxy-*m*-ditolyl separated in crystalline form. The reaction was not as clean as in the cases in which the absolute alcohol was used, the solution becoming more deeply colored and the product more impure.

Eighteen grams of the salt were treated with methyl alcohol diluted with 10 per cent of its volume of water and the decomposition effected as before. The results were in every way similar. The yield was 4.5 grams of the ether.

After this, many other similar experiments were carried on. The water solution of the salt, after the diazotization was completed, was added to ten times its volume of methyl alcohol and the salt decomposed in the usual manner. The per-

centage of the ether obtained was in every case nearly the same. When, however, the alcohol contained as much as 40 or 50 per cent of water, the yield of the ether was materially diminished and the formation of tarry products relatively greater. In all cases of dilution the product was not as pure as when the absolute alcohol was used, so that, although the yield of the ether was not materially better when the absolute alcohol was employed, than in those cases when the alcohol was diluted to within 20 per cent of its volume with water, yet the absolute alcohol method proved to be the best, as the excess of alcohol was ready for another decomposition as soon as distilled off, and the reaction by this method was cleaner in every way. I decomposed in this way 180 grams of the tetra-zonium salt and obtained a yield of 42 grams of the crude ether, which, when purified, gave 33 grams of pure dimeth-oxy-*m*-ditolyl.

Decomposition of the Tetrazonium Chloride with Ethyl Alcohol.—The decomposition was carried on at the boiling temperature of the alcohol. Throughout the operation aldehyde was given off. On allowing the alcoholic solution to cool, crystals were obtained which resembled those obtained by the decomposition with methyl alcohol. From 20 grams of the salt 2.25 grams of the crude product were obtained. The alcohol was then distilled off and six times its volume of a saturated solution of sodium chloride added, but nothing was obtained in this way. The tarry oil in the distillation-flask was then subjected to distillation with steam, and a few drops of a yellow oil were obtained. These experiments were repeated many times, and the yields were relatively the same in every case. The amount of the oil formed was never determined accurately, but it appeared to be produced in nearly the same amount as the crystalline solid. It is very difficultly volatile with water vapor. Its density is about the same as that of water. After a sufficient quantity of it had been obtained, it was taken up from the water with ether, dried with calcium chloride, and subjected to distillation. It passed over almost wholly at 280° to 281°, and was recognized as *m*-ditolyl, which has a specific gravity of 0.9993 at 16°. This

substance was discovered by Schultz,[1] in 1884, as one of the products of the action of nitrous acid on an alcoholic solution of *o*-tolidine. He described it as a yellow oil boiling at 281°, which, by oxidation with potassium bichromate and sulphuric acid, yields isophthalic acid. By careful oxidation in acetic acid solution with the calculated amount of chromic acid he obtained a new acid, diphenyldi-*m*-carboxylic acid, melting at 193°. In 1888 Stalle[2] repeated the experiments of Schultz, and made many derivatives of this hydrocarbon. He found 289° to be its boiling-point. A little later Perrier[3] succeeded in oxidizing one of the methyl groups by means of nitric acid (sp. gr. 1.14), and thus obtained the monocarboxylic acid.

The crystalline solid, which had been obtained in the decomposition described above, was dissolved in alcohol and decolorized with animal charcoal. It is not as soluble in alcohol as is the product obtained from the reaction of methyl alcohol with the diazo compound, and the difference in solubility at the boiling temperature and a few degrees below is even more marked than is this difference in the case of dimethoxy-*m*-ditolyl. It is insoluble in water, practically insoluble in cold alcohol and ether. When the alcoholic solution is allowed to cool it crystallizes therefrom in beautiful pearly plates, melting sharply at 154°. This compound was therefore supposed to be diethoxy-*m*-ditolyl, first obtained by Schultz by the action of nitrous acid on an alcoholic solution of *o*-tolidine. He gives its melting-point as 156°. About two years later the same substance was made by Hobbs,[4] by treating the potassium salt of dihydroxy-*m*-ditolyl with ethyl iodide.

I. 0.2000 gram substance gave 0.5885 gram CO_2 and 0.1450 gram H_2O.

II. 0.2000 gram substance gave 0.5916 gram CO_2 and 0.1451 gram H_2O.

III. 0.2000 gram substance gave 0.5886 gram CO_2 and 0.1444 gram H_2O.

[1] Ber. d. chem. Ges., **17,** 468.
[2] *Ibid.*, **21,** 1096.
[3] Compt. rend., **114,** 484.
[4] Ber. d. chem. Ges., **21,** 749.

	Calculated.	I.	Found. II.	III.
C	80.0	80.25	80.70	80.30
H	8.1	8.05	8.10	8.00
O	11.9	....	....	....

Thus it is seen that when the tetrazonium chloride is decomposed with methyl alcohol the "alkoxy" reaction only takes place, while, when the decomposition is effected with ethyl alcohol, both the " hydrogen" and the " alkoxy" reactions take place. The latter decomposition is not as clean as the former, and the definite products are not formed in as large quantity.

Decomposition of the Tetrazonium Salt with Ethyl Alcohol under Varying Conditions of Temperature and Dilution of the Alcohol.—Some of the salt was allowed to stand in contact with absolute ethyl alcohol for two weeks. The odor of aldehyde was noticeable at any time if the mixture was shaken up, but at the end of this time the greater part of the salt was still undecomposed. The flask containing the partially decomposed salt was attached to a return-condenser and the alcohol heated to boiling, when the nitrogen was evolved and the decomposition completed. The diethoxy-*m*-ditolyl and *m*-ditolyl were separated as before and their relative amounts were the same as previously found.

The decomposition was next effected with ordinary 95 per cent alcohol by the usual method of heating the alcohol to boiling. The yields were the same.

Many experiments were carried on with various dilutions, as the result of which it was found that the relative amounts of the oil and crystalline solid were not materially affected by diluting the alcohol with water up to 20 per cent of its volume, and also that the total yields were about the same. The reaction in these cases seemed very nearly as clean as when the absolute alcohol was used. When the alcohol was diluted with more than 20 per cent of its volume of water the yields diminished, and with increasing dilution the reaction was less clean and the amount of tar formed greater. Most of the diethoxy-*m*-ditolyl used in this investigation was obtained as a

by-product in the preparation of dimethoxy-*m*-ditolyl. The alcohol-water mixture, from which most of the tetrazonium chloride had been precipitated, was poured into a flask and the salt therein remaining decomposed by heating the solution on a water-bath. Half of the alcohol was then distilled off and the solution allowed to cool, when the diethoxy-*m*-ditolyl crystallized out. No effort was made to separate the *m*-ditolyl because another method of making this compound was discovered by which it could be obtained in any desired amount and in almost quantitative yield. Our attention was next turned to the action of nitric acid on the two phenol ethers which had been made.

Action of Nitric Acid on Dimethoxy-m-ditolyl and on Diethoxy-m-ditolyl.—Ordinary concentrated nitric acid converts dimethoxy-*m*-ditolyl into a tetranitro product that crystallizes in needles and melts at 130°.5. Estimations of nitrogen gave 13.5, 13.24, and 13.4 per cent. The calculated percentage for a tetranitro product is 13.27.

Fuming nitric acid gave the best results in the case of diethoxy-*m*-ditolyl. The product crystallizes in rhombs or needles resembling dinitrobenzene. It melts at 142°. Nitrogen found 12.9, 12.5, and 12.6 per cent. Calculated 12.44 per cent.

Preparation of Dihydroxy-m-ditolyl, or o-Dicresol.—In 1888 Gerber[1] and Hobbs[2] prepared this substance by boiling a water solution of metaditolyltetrazonium chloride, and obtained it in the form of large, broad needles, melting at 157°. It was found that unless the solution was very dilute, very little of the *o*-dicresol was formed and that a few drops of sulphuric acid increased the yield. I will describe one experiment, in which the proportions were such as to give the best results. Ten grams of tolidine hydrochloride were diazotized in the usual manner. The water solution of the diazo compound was poured into a 3-liter flask and 1500 cc. of water were added. After the addition of a few drops of sulphuric acid the whole was boiled for fifteen minutes. On cooling,

[1] Ber. d. chem. Ges., **21**, 749.
[2] *Ibid.*, **21**, 1065.

the tar formed became attached to the sides of the flask, and from the clear solution the *o*-dicresol was obtained in the form of large, broad needles. The yield was 2.5 grams. The crystals were further purified by recrystallization from boiling water and melted sharply at 155°. *o*-Dicresol is very soluble in alcohol and remains in solution as long as any alcohol is present, but when the alcohol has all evaporated the substance is obtained in the form of plates, always of a brownish color. A water-alcohol mixture was found to be an excellent solvent for *o*-dicresol, from which it crystallizes in needles perfectly white.

This substance was also prepared by the method of Graebe by the action of halogen acids on phenol ethers in sealed tubes at high temperatures.

Action of Sodium Methylate on the Tetrazonium Compound.— Twenty grams of the tetrazonium chloride were decomposed by a solution of sodium methylate in methyl alcohol. The sodium methylate was made by dissolving 15 grams of clean, bright, metallic sodium in 250 cc. of absolute methyl alcohol, the alcohol being kept in ice-water while the reaction was taking place. This solution was used for the decomposition of the tetrazonium compound, being kept in ice-water all the while. The tetrazonium compound was added in small portions from time to time and the mixture well shaken. The action took place energetically, nitrogen being freely evolved. For the decomposition of 20 grams of tetrazo compound about fifteen minutes were required, the temperature being kept below 20°. The solution turned red at first, and finally almost black, and much matter of a tarry nature separated. After the decomposition was complete the methyl alcohol was distilled off and the contents of the flask subjected to steam-distillation. Drops of an oil were thus carried over. This was taken up in ether, dried, and distilled. It was easily recognized as *m*-ditolyl. This oil is not very volatile with steam and it is almost impossible to separate all of it from the tar by this means. The yield of the crude *m*-ditolyl was 5 grams.

Action of Methyl Alcohol on the Tetrazonium Compound in

the Presence of Sodium Hydroxide.—Twenty grams of the tetrazonium chloride were decomposed with 200 cc. of absolute methyl alcohol, in which 10 grams of sodium hydroxide had been dissolved. As before, the alcohol was cooled with ice and the tetrazonium compound added in small portions. The reaction proceeded exactly as in the preceding experiment, being very energetic, almost violent at first. As soon as the reaction was complete the alcohol was distilled off, and the residue distilled in steam. *m*-Ditolyl passed over with the steam, which was separated from the water with ether. Five and a half grams were thus obtained. In both of these experiments, as was to be expected from earlier work in this laboratory, the " hydrogen" reaction took place. A careful search was made for any ether that might have been formed at the same time, but the search was fruitless.

Action of Methyl Alcohol on the Tetrazonium Compound in the Presence of Zinc Dust.—Ten grams of the tetrazonium compound were placed in a flask containing 10 grams of zinc powder and 100 cc. of absolute methyl alcohol. There was no immediate action, though the solution darkened gradually, and on shaking a slight evolution of nitrogen was observed, but the decomposition was very slow. After standing for twenty-four hours most of the tetrazonium compound remained undecomposed. The flask containing the mixture was then attached to a return-condenser and heated upon a water-bath. The decomposition proceeded smoothly and the reaction was soon over, the alcohol being of a light-yellow color. This was filtered to remove the zinc dust and then the methyl alcohol distilled off. There remained in the distillation-flask a dark-red oil, which was distilled in steam and separated from the water with ether. The yield from 10 grams of the tetrazonium compound was 4.5 grams of crude *m*-ditolyl. In this decomposition there was no formation of anything of a tarry nature and the reaction was perfectly clean. In this, as in the decompositions in the presence of sodium hydroxide and sodium methylate, a strong odor resembling aldehyde was noticed, which was probably paraldehyde. When 10 grams of the tetrazonium compound were

decomposed with ethyl alcohol in the presence of zinc dust
the decomposition took place in exactly the same manner.
At the end of the operation the solution cleared up to a straw
color, as before.   The yield of *m*-ditolyl from 10 grams of the
tetrazonium compound was 4 grams.   It was thought advisa-
ble to make quite a quantity of *m*-ditolyl and repeat, to some
extent, the experiments of Schultz.

One hundred grams of tolidine hydrochloride were diazo-
tized, and the tetrazonium salt precipitated, filtered, washed,
and dried in the usual manner.   It was then decomposed with
methyl alcohol in the presence of zinc dust.   The clear, yel-
low solution thus obtained was filtered from the zinc and the
alcohol distilled off.   A considerable amount of the reddish
oil remained in the flask.   To the water-alcohol mixture from
which the tetrazonium compound had been precipitated and
which was already of a reddish color, zinc dust was added, the
flask attached to a reflux-condenser, and the mixture boiled.
The decomposition of the tetrazonium compound therein re-
maining was thus effected, and the solution cleared up to a
light-yellow color.   The zinc dust was filtered off and most of
the alcohol removed by distillation, when an oil separated. This
was removed by means of a separating-funnel and added to
that obtained from the decomposition with absolute methyl
alcohol and zinc dust.   The oil was then taken up in ether,
dried with calcium chloride, and distilled from a flask of ap-
propriate size.   Forty-eight grams of *m*-ditolyl, boiling at
278° to 281°, were thus obtained.   The yield of the pure sub-
stance is thus 76 per cent of the theoretical amount.   The
real yield was even greater than this, the operation being at-
tended with considerable loss.   After all of the *m*-ditolyl had
distilled off, the thermometer rose rapidly to 360°, above which
point a few drops of an oil of a strong odor passed over, but it
was obtained in so small quantity that no attempt was made
to find out what it was.

The decomposition of the tetrazonium chloride with the
alcohols in the presence of zinc dust furnishes a very satisfac-
tory method for the preparation of *m*-ditolyl.   The manipula-

tion is very simple and the yield excellent. Heretofore there have been three methods for its preparation :

1. Heating *o*-dicresol with zinc powder.

2. Conversion of dichlor-*m*-ditolyl into *m*-ditolyl by sodium amalgam in alcoholic solution, sodium in solution in amyl alcohol or zinc and hydrochloric or acetic acid.

3. By the action of nitrous acid on an alcoholic solution of *o*-tolidine. This method was discovered by Schultz and used by him and Stolle in their investigations on *m*-ditolyl, being the most satisfactory and economical method of the three. The yields of *m* ditolyl, as given by these investigators, were never as much as 25 per cent of the theoretical amount.

Several subsequent experiments of mine have shown that a very satisfactory, and perhaps the most useful, method for the preparation of *m*-ditolyl is the decomposition of tetrazonium chloride with ordinary 98 per cent alcohol in the presence of zinc dust, the separation of the *m*-ditolyl being accomplished as described above. A yield of 75 per cent of *m*-ditolyl can be very easily obtained in this way.

Oxidation of m-Ditolyl.—According to Schultz and Stolle, when *m*-ditolyl is oxidized with potassium bichromate and sulphuric acid, the product is isophthalic acid. I attempted to reach this result by using the proportions generally used in such cases, and the acid diluted with 2 volumes of water. After boiling several hours the oxidation had taken place only very slightly. It was found that this oxidation is best effected by using acid diluted to just half its volume with water and about six times the calculated amount of potassium bichromate. The oxidation proceeds smoothly after the first violent reaction is over. After two hours' boiling of the mixture the oxidation is practically completed. After cooling, the solid was filtered off, washed with cold water, dissolved in a dilute solution of sodium carbonate, and the solution of the sodium salt formed decolorized with animal charcoal. On the addition of hydrochloric acid the isophthalic acid was precipitated perfectly white. This was crystallized from water and its melting-point taken. The yield of isophthalic acid by this method was very good. Five grams of *m*-ditolyl were dis-

solved in glacial acetic acid and the calculated amount of
chromic acid for its total conversion to diphenyldi-*m*-carboxylic
acid was added, this, also, in acetic acid solution.   The ac-
tion was quite violent at first, but soon moderated.   This solu-
tion was then poured into a flask attached to a reflux-con-
denser and boiled for several hours.   Most of the acetic acid
was then distilled off and water added, when a slight precipi-
tation of the desired acid resulted, which was filtered, washed
with water, and recrystallized until the melting-point became
constant.   The acid melts at 190°.5.   For the oxidation of
m-ditolyl, in repetition of Perrier's work, with nitric acid (sp.
gr. 1.14), four days were necessary, the acid being boiled
continually.   On cooling, a white substance separated which
was dissolved in a dilute solution of sodium carbonate, pre-
cipitated with hydrochloric acid, and recrystallized from a
water-alcohol mixture.   It was recognized by its melting-
point (202°) as the acid obtained by Perrier.

It was thought advisable to try the action of potassium per-
manganate as an oxidizing agent on *m*-ditolyl, but this
powerful reagent was unable to overcome the resistance of
this hydrocarbon to oxidation.   A neutral solution of the per-
manganate was first used, but no oxidation resulted.   The
action of the permanganate was next tried in potassium hy-
droxide solutions of many concentrations, but the *m*-ditolyl
was never oxidized.   This oxidation was attempted at the
temperature of the boiling-point of water.   A slight addition
of the permanganate gave the solution a color which hours of
heating, in contact with the hydrocarbon, did not remove.
m-Ditolyl resists most strongly all oxidizing agents.   The
only one which gave good results was a mixture of potassium
bichromate and sulphuric acid, which oxidizes the hydrocar-
bon to isophthalic acid.

*Action of Normal Propyl Alcohol on the Tetrazonium Chlo-
ride.*—The tetrazonium compound was decomposed with
propyl alcohol under different conditions.   In the first case,
13 grams of the tetrazonium compound were placed in a small
flask and 200 cc. of the alcohol added.   The flask was at-
tached to a return-condenser and heated in a water-bath, in

which the water was briskly boiling. It was afterwards found best to heat the flask, placed on a wire gauze and attached to a return-condenser, with a small flame until the reaction begins. The flame is then removed and the reaction proceeds smoothly, the heat generated thereby being almost sufficient to carry it to completion. A little further heating completes the reaction and clears the solution up to a wine color. From 13 grams of the tetrazonium compound a little over 3 grams of *m*-ditolyl, or 40 per cent of the theoretical amount, were obtained. Other experiments showed that the yield of the *m*-ditolyl by this method was at least 45 per cent of the theoretical amount.

Eleven grams of the tetrazonium compound were decomposed in exactly the same manner, except that 10 grams of zinc powder were added. The decomposition was rather more energetic than before, the solution clearing up at the end of the operation to an amber color. On filtering off the zinc dust and evaporating the alcohol a dark-colored oil was left, and as in all cases in which zinc dust had been used, there was a total absence of the formation of any tarry products. The oil remaining was taken up in ether, dried with calcium chloride, and distilled. A little less than 4 grams of *m*-ditolyl were thus obtained, or a yield of at least 60 per cent of the theoretical amount.

The addition of sodium hydroxide to the propyl alcohol caused the decomposition to take place at room temperature very rapidly. Tarry products were formed in abundance, and the reaction that took place was the "hydrogen" one, though the yield was not good.

In none of the decompositions with propyl alcohol did the "alkoxy" reaction take place at all. The "hydrogen" reaction, and that alone, takes place when tetrazo-*m*-ditolyl chloride is decomposed with propyl alcohol.

Preparation of Diphenyltetrazonium Chloride.—The benzidine hydrochloride used in these experiments was prepared thus: One hundred grams benzidine were mixed with 600 cc. water in a large evaporating dish and the mixture heated almost to the boiling-point of water. Hydrochloric acid was

now added in slight excess when all the benzidine dissolved, forming a red solution. This was easily decolorized by animal charcoal. To the colorless solution about one-fourth of its volume of strong hydrochloric acid was added with stirring, when the *p*-benzidine hydrochloride was precipitated in the form of a colorless, fine, crystalline mass. The hydrochloride obtained by this method is almost perfectly pure, as the hydrochlorides of the isomeric benzidines remain in solution. This was filtered off as dry as possible with the aid of a Büchner funnel and filter-pump, and was then, while still slightly moist, bottled and used in that condition, as this was found to be favorable for the formation of the tetrazonium compound.

As in the diazotization of tolidine hydrochloride, a paste of the salt and water was used. In this case it was found more necessary to keep the paste of the hydrochloride and water at a low temperature than was the case with tolidine hydrochloride. To accomplish this the oxides of nitrogen, formed in the usual manner, were passed through a Woulff's bottle, and then the cooled gases were led into a cylinder, which contained the paste of the benzidine hydrochloride and water, and was surrounded with ice. In order to diazotize the hydrochloride completely, about 3 parts of water are necessary to 1 of the salt. For the precipitation of the tetrazonium compound, six times the volume of the water solution of the tetrazonium compound of ordinary alcohol is required. This is previously cooled to as low a temperature as a freezing-mixture can cool it, and poured into the solution. A precipitation in the form of beautiful needles at once takes place. The vessel containing this mixture is then allowed to stand in the freezing-mixture for some time and the tetrazonium compound is then filtered off. If the diazotization has been successful and the water solution is of a light straw color, as it should be, the crystals of the tetrazonium chloride are almost perfectly white. Unfortunately, even if one works with the greatest care, this result is not generally reached, but if attention is paid especially towards keeping the temperature of the paste which is being diazotized below

5°, and the alcohol for precipitation is cold, a good quality of tetrazonium compound will be obtained. The diazotization is best effected by means of a rapid current of the oxides of nitrogen, and, indeed, this is necessary for a successful operation, which is best carried through in from twenty to twenty-five minutes. My early attempts at making this tetrazonium compound were failures, because the current of gases was too slow and the operation took too long a time. Diphenyltetrazonium chloride is a rather heavy substance, settling rapidly to the bottom of the beaker in which it is formed. When it is filtered, washed with alcohol and ether, and dried, it can be handled safely, although it is not as stable a compound as ditolyltetrazonium chloride. The yield of the diazo compound by this method is about 85 per cent of the theoretically possible amount. The change of color during diazotization is not so marked as in the case of the diazotization of tolidine hydrochloride. When the gases are first passed into the mixture a slightly brownish discoloration takes place, which increases slowly until the end of the operation. Then it clears up to a light-yellow, when the operation proceeds best. The greatest care is necessary in keeping all of the solutions, at every stage of the operation, at a low temperature. An important point of difference between *m*-ditolyltetrazonium chloride and diphenyltetrazonium chloride is observed when the two are allowed to stand in contact with alcohol at room temperature. The former is decomposed very slowly, while the latter is easily decomposed, especially if the alcohol is largely diluted with water, in which case tarry products are largely formed. If the same decomposition is effected at the boiling-point of the alcohol the reaction is much cleaner.

Action of Methyl Alcohol on Diphenyltetrazonium Chloride.— Twenty grams of the tetrazonium compound were placed in a 2-liter flask and 300 cc. of absolute methyl alcohol poured over the salt. If this mixture is allowed to stand, gradual decomposition will ensue, but the action will be incomplete and results unsatisfactory. The amount of tarry matter formed will be much larger than if the decomposition is carried on at a higher temperature. When the flask containing the mixture

of the tetrazonium salt and alcohol is attached to a reflux-condenser and heated on a water-bath the reaction is very satisfactory, provided certain precautions are taken. There will be little evolution of nitrogen until the boiling-point of the alcohol is almost reached. As soon as the evolution of nitrogen begins the flame should be removed and the action quickened by shaking the contents of the flask. The reaction proceeds smoothly. When the evolution of nitrogen almost ceases, the mixture is heated to boiling for fifteen minutes to complete the reaction. The resulting solution is of a light reddish color and the reaction is quite clean. The methyl alcohol is then distilled off and 6 volumes of a saturated solution of sodium chloride added to the distillate, when the solution becomes slightly cloudy. This was shown to be due to a trace of diphenyl, formed in the reaction. After distillation of the methyl alcohol there remains in the flask a yellow solid, which seems to contain very little matter of a tarry nature. This is broken up, a little water added, and distillation with steam carried on, when a nearly inappreciable amount of a white solid, melting at 68°, is carried over by the steam, which by its melting-point and odor is recognized as diphenyl. The yellow solid remaining in the flask, which is not volatile with water vapor, is then dissolved in ordinary alcohol, in which it is difficultly soluble at its boiling temperature and insoluble in the cold. As in the case of the two phenol ethers, which have already been described, this substance shows a marked difference in its solubility in alcohol at its boiling temperature, and a few degrees below that temperature. The alcoholic solution was then decolorized by boiling with animal charcoal for a few minutes, and on cooling, beautiful plates of a pearly luster were obtained. In this first experiment the yield was 8 grams. When the substance was a second time crystallized the melting-point was sharp at 172°.

Two analyses gave the following results :

I. 0.2000 gram substance gave 0.5775 gram CO_2 and 0.1193 gram H_2O.

II. 0.2000 gram substance gave 0.5751 gram CO_2 and 0.1181 gram H_2O.

	Calculated.	I.	II.
		Found.	
C	78.50	78.75	78.43
H	6.54	6.62	6.56
O	14.96	....	....

The yield of diphenyl, by the action of methyl alcohol on the tetrazonium salt, is very small. The reaction that takes place is the "alkoxy." The largest yields obtained range from 65 to 70 per cent of the theoretical. Dimethoxydiphenyl is insoluble in water, difficultly soluble in alcohol and ether. In alcohol it is not as soluble as are dimethoxy- and diethoxy-*m*-tolyl.

Decomposition of Diphenyltetrazonium Chloride with Methyl Alcohol under Different Conditions.—Sixteen grams of the tetrazonium salt were placed in a flask and 250 cc. methyl alcohol added. Fifteen grams of zinc dust were now introduced and the tetrazonium compound decomposed in the usual way. The decomposition began when the alcohol had almost reached its boiling temperature. It then proceeded smoothly, as in the preceding experiment. The flame was removed as soon as the reaction began, and the heat generated by the reaction was almost sufficient to complete it. In order to be perfectly sure that the reaction was complete, the solution was boiled for a few minutes. The yellow solution resulting was now filtered to remove the zinc dust and the alcohol was distilled off. A portion of the distillate was treated with 6 volumes of a standard solution of sodium chloride, but only a slight precipitation resulted. After this the alcoholic distillate was not treated with sodium chloride, but was preserved for use in other decompositions, as the phenol ether is not volatile with alcohol vapor, and diphenyl only to a very small extent. In this experiment 6.5 grams diphenyl, or 73 per cent of the theoretical yield, were obtained. The brownish residue in the distillation-flask was dissolved in alcohol and carefully examined for dimethoxydiphenyl, but none was found. During the decomposition a strong odor, resembling that of aldehyde, was noticed. As in all other decompositions recorded in which zinc dust was used, the reaction was

practically clean and the presence of the zinc dust determined the "hydrogen" reaction.

Decompositions of diphenyltetrazonium chloride with sodium methylate and with methyl alcohol in the presence of sodium hydroxide were also carried out, but only small amounts of the compound were thus decomposed, the object being simply to find out which way the reaction takes place. The decompositions proceeded in exactly the same way in both cases. In both cases diphenyl was formed. No dimethoxydiphenyl was obtained. The "hydrogen" reaction takes place when diphenyltetrazonium chloride is decomposed with methyl alcohol in the presence of zinc dust, sodium methylate, or sodium hydroxide.

Action of Nitric Acid on Dimethoxydiphenyl.—The best yield was obtained by the use of fuming nitric acid. The product crystallizes from alcohol in beautiful, straw-colored needles, which melt sharply at 244°.6. Three determinations of nitrogen gave as the percentage of that element in the substance 14.6, 14.1, and 14.5, which agree quite well with the formula $C_{14}H_{10}O_2(NO_2)_4$, for which the percentage of nitrogen is 14.22.

Action of Diphenyltetrazonium Chloride on Ethyl Alcohol.—Twenty-three grams of the tetrazonium salt were placed in a 2-liter flask and 300 cc. of absolute ethyl alcohol poured over it. The flask was then attached to a reflux-condenser and heated on a water-bath. The heating of this mixture for the decomposition of the tetrazonium compound requires the greatest care, and special precautions must be taken. Near at hand, a water-bath containing cold water, is placed. The mixture is well shaken while the heating is going on and carefully watched. The reaction does not begin until the boiling temperature of the alcohol is almost reached. As soon as evidences of decomposition are observed the flame is removed, the water-bath containing hot water is taken away. The mixture is now shaken and the decomposition proceeds rapidly. When it increases in violence, the flask is plunged in the cold water and kept there until the action moderates, when it is removed. These operations are repeated until the reaction is over and

all of the compound has gone into a reddish-yellow solution. This is then heated and the alcohol boiled for a few minutes. Throughout the operation the strong odor of aldehyde is noticeable, and it is evident that the reaction that takes place is to a large extent the "hydrogen" one. The first decompositions of this tetrazonium chloride with ethyl alcohol were carried on in the same manner as those with methyl alcohol, and the violence of the reaction was so great that the greater part of the reacting mixture was projected through the condenser-tube across the room. In several subsequent experiments, in which the special precautions were not observed, a considerable loss was occasioned by the same violence. The method described above is that by which the best results were obtained. In the experiment described, the red solution of the decomposition-products was subjected to distillation and all of the alcohol removed in this way. A reddish oil remained, which, on cooling, solidified to a reddish, crystalline mass. The alcoholic distillate was tested by adding to it several volumes of a saturated solution of sodium chloride, when a small quantity of a white solid was precipitated. The rest of the alcohol was not treated in the same way, because the substance was only slightly volatile with alcohol vapor, but was preserved for other decompositions. The reddish residue in the distillation-flask was distilled in steam, and most of it passed over with the water vapor as a white, crystalline solid, having the strong odor of diphenyl and melting, when crystallized from alcohol, at 68°.

The yield was 10.25 grams, or over 80 per cent of that theoretically possible.

I. 0.2000 gram substance gave 0.6841 gram CO_2 and 0.1179 gram H_2O.

II. 0.2000 gram substance gave 0.6825 gram CO_2 and 0.1171 gram H_2O.

	Calculated.	I.	II.
		Found.	
C	93.51	93.30	93.07
H	6.49	6.55	6.50

Thus it is seen that the substance formed by the action of

diphenyltetrazonium chloride on ethyl alcohol is diphenyl, and that the " hydrogen" reaction alone takes place in this case. As benzidine is easily obtained, and these reactions take place easily, this furnishes the best method at present known for the preparation of diphenyl.

Decomposition of Diphenyltetrazonium Chloride with Ethyl Alcohol under Different Conditions.—As in the decompositions described, extreme care was necessary to prevent the reaction from taking place with too much violence. Decompositions were carried on with absolute, 95 per cent alcohol, and alcohol still more dilute in the presence of zinc dust, which was added in about the same amount as the tetrazonium compound. It was found that, as long as the alcohol did not contain more than 15 per cent of water, the decompositions proceeded like those with absolute ethyl alcohol alone. Under proper conditions the reaction was smooth and the decomposition perfectly clean, no tarry products being formed, and the solution clearing up at the end of the operation to a straw color. The zinc powder was now removed by filtration, the yellow solution decolorized with animal charcoal, and evaporated until crystallization took place. Diphenyl was obtained perfectly pure by recrystallizing this product from ordinary alcohol. The yield by this method is from 80 to 85 per cent of the theoretical amount. When the alcohol contains more water than 15 per cent, tarry products are formed, the amount being greater the greater the dilution of the alcohol, and the amount of diphenyl relatively smaller. Sodium hydroxide, added to ethyl alcohol, used for the decomposition of diphenyltetrazonium chloride, causes a violent reaction to take place at room temperature, and a freezing-mixture is required to keep the reaction within bounds. A large amount of tarry products separates, and the diphenyl is removed by distilling off the alcohol and distilling the tarry residue in steam. For a laboratory method for the preparation of diphenyl, I would suggest the decomposition of diphenyltetrazonium chloride with ordinary alcohol in the presence of zinc dust. In all cases in which the tetrazonium chloride was decomposed with ethyl alcohol diphenyl alone was formed.

Action of Normal Propyl Alcohol on Diphenyltetrazonium Chloride.—Twelve grams of the tetrazonium chloride were placed in a half-liter flask and 150 cc. of propyl alcohol added. At room temperature there was practically no action, although when the mixture was allowed to stand for several hours the alcohol became colored reddish. The flask was attached to a reflux-condenser and the alcohol heated to its boiling temperature with a small flame. As soon as the decomposition began the flame was removed and the decomposition allowed to proceed. When the nitrogen almost ceased being given off, the alcohol was boiled for a few minutes and then distilled off. There remained a brownish residue, which was subjected to distillation in steam. A little over 3 grams of diphenyl were thus obtained. This experiment, repeated many times, showed that the yield of diphenyl was between 40 and 50 per cent of the theoretical. When the steam distillation was completed some tarry matter remained in the flask, from which nothing of value was ever obtained. When the tetrazonium compound was decomposed with propyl alcohol in the presence of an excess of zinc dust, the reaction took place in the same manner, but was much cleaner, and the amount of tarry products smaller. By this method the yield of diphenyl was brought up to 60 per cent of the theoretical. The addition of sodium hydroxide to the propyl alcohol used for this decomposition caused the reaction to take place at room temperature and diphenyl was formed, together with much tarry matter. As was found in the case of the decomposition of ditolyltetrazonium chloride with propyl alcohol, so in the case of the decomposition of diphenyltetrazonium chloride with the same alcohol, the "hydrogen" reaction alone took place.
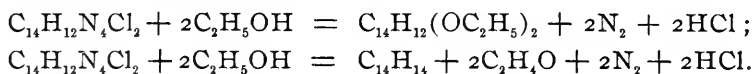
Summary of Experimental Work.

Ditolyltetrazonium chloride, when decomposed with methyl alcohol, yields as the only product dimethoxy-*m*-ditolyl, or the "alkoxy" reaction alone takes place:

$$C_{14}H_{12}N_4Cl_2 + 2CH_3OH = C_{14}H_{12}(OCH_3)_2 + 2N_2 + 2HCl.$$
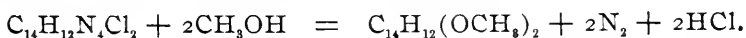
When the same tetrazonium compound is decomposed with

ethyl alcohol the products of the reaction are *m*-ditolyl and diethoxy-*m*-ditolyl, and these products are formed in approximately equal amounts, or both the "alkoxy" and the "hydrogen" reactions take place :

$$C_{14}H_{12}N_4Cl_2 + 2C_2H_5OH = C_{14}H_{12}(OC_2H_5)_2 + 2N_2 + 2HCl ;$$
$$C_{14}H_{12}N_4Cl_2 + 2C_2H_5OH = C_{14}H_{14} + 2C_2H_4O + 2N_2 + 2HCl.$$

When the same tetrazonium compound is decomposed with normal propyl alcohol the only product isolated was *m*-ditolyl, or the "hydrogen" reaction alone takes place :

$$C_{14}H_{12}N_4Cl_2 + 2C_3H_7OH = C_{14}H_{14} + 2C_3H_6O + 2N_2 + 2HCl.$$
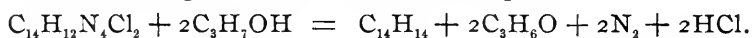
When the same tetrazonium compound was decomposed with a solution of sodium methylate in methyl alcohol, the "hydrogen" reaction alone took place. The same reaction was found to take place when the tetrazonium compound was decomposed with each alcohol, in turn, in the presence of sodium hydroxide or zinc powder.

When diphenyltetrazonium chloride is decomposed with methyl alcohol the product is dimethoxydiphenyl, and at the same time a trace of diphenyl is formed, the "alkoxy" reaction taking place almost exclusively :

$$C_{12}H_8N_4Cl_2 + 2CH_3OH = C_{12}H_8(OCH_3)_2 + 2N_2 + 2HCl.$$
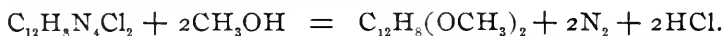
The decomposition of the same tetrazonium compound with ethyl alcohol gives only diphenyl, or the "hydrogen" reaction alone takes place :

$$C_{12}H_8N_4Cl_2 + 2C_2H_5OH = C_{12}H_{10} + 2C_2H_4O + 2N_2 + 2HCl.$$
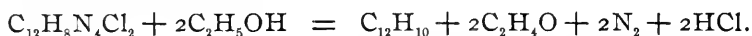
The same tetrazonium compound, decomposed with normal propyl alcohol, yields only diphenyl or the "hydrogen" product :

$$C_{12}H_8N_4Cl_2 + 2C_3H_7OH = C_{12}H_{10} + 2C_3H_6O + 2N_2 + 2HCl.$$
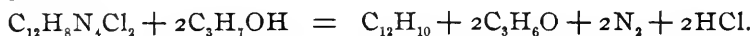
Sodium methylate, in methyl alcoholic solution, yields only diphenyl.

When the tetrazonium compound is decomposed with methyl, ethyl, or propyl alcohol in the presence of sodium hydroxide, or zinc powder, the "hydrogen" reaction alone takes place.

SOME Δ_2-KETO-R-HEXENE DERIVATIVES.

By James B. Garner.

A study of the reactions which might be brought about between benzoin and unsaturated aldehydes, ketones, and esters through the agency of cold ($15°$ C.) alcoholic sodium ethylate, was begun several years ago.[1] At that time it was found that benzoin is added to benzalacetone giving rise to a 1,5-diketone which, by loss of water and ring formation, is converted into 3,4,5-triphenyl-4-oxy-Δ_2-keto-R-hexene. This substance had previously been prepared by Professor Alexander Smith,[2] using potassium cyanide as condensing agent.[3] When sodium ethylate is used as condensing agent, the yield is much greater, the reaction takes place more smoothly, and the product formed is purer than when potassium cyanide is used. Knovenagel has made an exhaustive study of the Δ_2-keto-R-hexene derivatives. He has found (1) that substances of the type of acetoacetic ether and aliphatic aldehydes,[4] and aromatic aldehydes,[5] condense in the presence of diethylamine or piperidine to form 1,5-diketones, and that these diketones, with loss of water and ring formation, are converted into Δ_2-keto-R-hexene derivatives; (2) that desoxybenzoin adds itself to substances of the type benzalacetylacetone, forming 1,5-diketones, which, by loss of water and ring formation, yield Δ_2-keto-R-hexene derivatives.

Recently the study has been extended to include the reactions which might take place between the ketols—benzoin, cuminoin, furoin, anisoin, and piperonoin—and the unsaturated ketones—benzalacetone, cuminalacetone, p-methoxybenzalacetone, and piperonylenacetone. In all the reactions, Δ_2-keto-R-hexene derivatives are formed, except in those in which furoin is used. Under no conditions has it been possible to bring about any interaction in any of the experiments in which furoin is used. All of the other reactions progress smoothly and excellent yields are obtained in each case. It

[1] Dissertation, Chicago, 1897, p. 17.
[2] Ber. d. chem. Ges., **26**, 65.
[3] This Journal, **22**, 250.
[4] Ann. Chem. (Liebig), **281**, 25 ; *Ibid.*, **288**, 321.
[5] *Ibid.*, **306**, 223.

has been ascertained also, that in place of the unsaturated ketone a mixture of the corresponding aldehyde and acetone may be used and the course of the reaction is in no way changed, but the yield is materially increased. To insure the completion of the reactions, however, it is necessary to boil the mixtures for fifteen minutes on the water-bath. An equal volume of a 10 per cent solution of sodium hydroxide may be used instead of the alcoholic sodium ethylate and the same reactions will take place but the yields are poorer.

In the present paper the study is limited to the consideration of only those cases which will, in a general way, indicate, (1) the nature of the products formed; and (2) the extent to which the reaction is applicable.

I. *Addition of Benzoin to Cuminalacetone.*

3,4-Diphenyl-5-cumyl-4-oxy-Δ_2-keto-R-hexene,

$$CH.C_6H_4.CH.(CH_3)_2$$

$C_6H_5.C.(OH).$ ⟋‾‾⟍ CH_2

$C_6H_5.C.$ ⟍__⟋ CO

CH
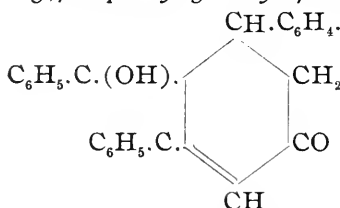
.—For the preparation

of this Δ_2-keto-R-hexene derivative, 1 molecule (6 grams) of benzoin is dissolved in boiling absolute ethyl alcohol (100 cc.), and to this solution is added 1 molecule (5.32 grams) of cuminalacetone. This mixture is treated with an alcoholic solution (4 cc.) of sodium ethylate (0.5 gram sodium in 30 cc. absolute ethyl alcohol). The mixture becomes deep-red in color, and upon standing in a cool place for two days deposits clusters of needle-like crystals. The crystalline mass is filtered off and after washing with absolute ethyl alcohol is recrystallized twice from glacial acetic acid. Clusters of long, fine, white needles result, which melt at 231°. It is insoluble in ligroin (40°–60°), ether, and cold alcohol, but dissolves readily in hot benzene, glacial acetic acid, and chloroform.

	Calculated for $C_{27}H_{26}O_2$.	Found.
C	84.80	84.67
H	6.81	6.92

If a mixture of one molecule each of cuminol (4.2 grams) and pure acetone (1.7 grams) is used instead of the cuminal-acetone, it has been established by several comparable experiments that it is necessary that the reaction shall be carried on at the temperature of the water-bath for fifteen minutes. Upon cooling the mixture, the Δ_2-keto-R-hexene derivative separates in a relatively pure condition. By repeated additions of 4 cc. of sodium ethylate at a time, additional quantities of the substance are obtained which make the yield almost quantitative. Experiments were made using the total quantity of sodium ethylate solution (12 cc.) required for the quantitative completion of the reaction, and it was found that the reaction took an entirely different course, resulting in the formation of the sodium ethylate addition-product of benzoin.[1]

The condensation takes place readily when 15 grams of a 10 per cent solution of sodium hydroxide are used in place of the 4 cc. of sodium ethylate solution.

Oxime of 3,4-Diphenyl-5-cumyl-4-oxy-Δ₂-keto-R-hexene,

$$CH.C_6H_4.CH.(CH_3)_2$$

$$C_6H_5.C.(OH). \quad CH_2$$

$$C_6H_5.C. \quad C=NOH$$

$$CH$$
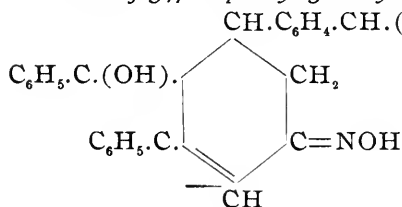
.—This oxime is obtained by boiling a mixture of 1 molecule (1 gram) of the Δ_2-keto-R-hexene derivative with 3 molecules (0.56 gram) of hydroxylamine hydrochloride and 1.5 molecules (0.56 gram) of sodium carbonate dissolved in ethyl alcohol (140 cc.) for forty-five minutes, using a return-condenser. One-half of the alcohol is distilled off and the residue, on cooling, deposits white crystals, which, when they have been recrystallized from a mixture of benzene and ligroin, melt at 221° to 223°. The substance is easily soluble in hot alcohol, cold ether, acetic acid, and hot benzene, but very sparingly soluble in hot ligroin (40° to 60°).

	Calculated for $C_{27}H_{27}O_2N$.	Found.
N	3.53	3.72

[1] Dissertation, Chicago, 1897, p. 4.

3,4-Diphenyl-5-cumylphenol Acetate,

$$C.C_6H_4.CH(CH_3)_2$$

```
C₆H₅.C        CH
       |  |
C₆H₅.C        C.O.COCH₃
        CH
```
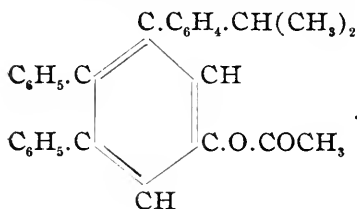
.—This body is prepared by boil-

ing the $\varDelta_2$-keto-R-hexene derivative with excess of either acetic anhydride or acetyl chloride for thirty minutes. The mixture assumes a yellowish-red tint, and yields a solid substance only when it is poured into a large excess of water. The white, amorphous mass recrystallizes from hot ligroin (40° to 60°) in bunches of long needles, melting at 98°. It is soluble in cold glacial acetic acid, benzene, ether, and alcohol, but is sparingly soluble in ligroin.

	Calculated for $C_{29}H_{26}O_2$.	Found.
C	85.72	85.50
H	6.40	6.62

3,4-Diphenyl-5-cumylphenol,

$$C.C_6H_4.CH(CH_3)_2$$

```
C₆H₅.C        CH
       |  |
C₆H₅.C        C.OH
        CH
```

.—
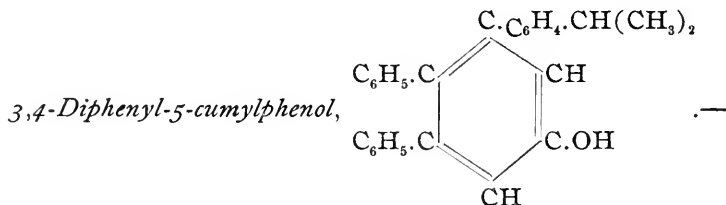
The acetate is boiled upon a water-bath with alcoholic potassium hydroxide for fifteen minutes. The mixture resulting is poured into excess of dilute hydrochloric acid, and a white mass is obtained. The amorphous phenol is recrystallized from hot alcohol. It forms white needles, which melt at 155°. It is readily soluble in cold chloroform, benzene, and ether, but sparingly soluble in hot ligroin (40° to 60°).

	Calculated for $C_{27}H_{24}O$.	Found.
C	89.00	88.96
H	6.60	6.87

II. Addition of Benzoin to Anisylideneacetone.

3,4-Diphenyl-5-anisyl-4-oxy-Δ₂-keto-R-hexene,

$$CH.C_6H_4(OCH_3)$$

$C_6H_5.C.(OH)$ ⟨hexagon ring⟩ $.CH_2$

$C_6H_5.C$ ⟨ring⟩ $.CO$

$.CH$
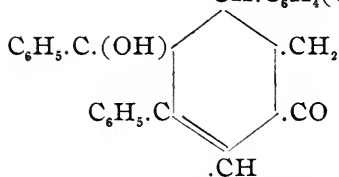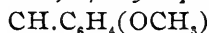
.—The 3,4-d i p h e n y l-5-anisyl-4-oxy-Δ₂-keto-R-hexene is prepared by the condensation of 1 molecule (6 grams) of benzoin, either with 1 molecule (5 grams) anisylideneacetone or with 1 molecule each of anisaldehyde (3.9 grams) and of pure acetone (1.7 grams) under exactly the same conditions which were used in the preparation of 3,4-diphenyl-5-cumyl-4-oxy-Δ₂-keto-R-hexene. The substance crystallizes in bunches of needles, either from hot glacial acetic acid or absolute alcohol, and melts at 233°.5. However the amount of alcohol required is large—for each gram 70 cc. of hot absolute alcohol are required. It is soluble in hot benzene and chloroform, but insoluble in ether and ligroin (40° to 60°). With cold concentrated sulphuric acid, a deep red coloration is produced.

	Calculated for $C_{25}H_{22}O_3$.	Found.
C	81.08	80.91
H	5.95	6.03

Oxime of the 3,4-Diphenyl-5-anisyl-4-oxy-Δ₂-keto-R-hexene.—For the preparation of the oxime a method, analogous to that described in the preparation of the oxime of 3,4-diphenyl-5-cumyl-4-oxy-Δ₂-keto-R-hexene, is used. After recrystallization from hot alcohol it melts at 196°. It is soluble in hot glacial acetic acid, chloroform, and benzene, but insoluble in ether and ligroin (40° to 60°).

	Calculated for $C_{25}H_{23}O_3N$.	Found.
N	3.63	3.85

Acetate of 3,4-Diphenyl-5-anisylphenol—This product is obtained by boiling the м₂-keto-R-hexene derivative with acetyl chloride on the water-bath for ten minutes. The mixture as-

sumes a deep red coloration. Nothing separates on cooling. When excess of water is added, however, an amorphous mass separates which, upon crystallization from hot ligroin (40° to 60°) or from aqueous alcohol, melts at 141° to 142°. It is soluble readily in cold benzene, ether, glacial acetic acid, and chloroform; sparingly soluble in hot benzene and aqueous alcohol.

	Calculated for $C_{27}H_{22}O_3$.	Found.
C	82.22	82.10
H	5.59	5.84

3,4-Diphenyl-5-anisylphenol.—The acetate, upon saponification with alcoholic potassium hydroxide, yields the phenol. The reaction requires only fifteen minutes' heating upon the water-bath to complete it. The product, which is obtained when the resulting solution is poured into dilute hydrochloric acid, is recrystallized from a mixture of alcohol and ligroin (40° to 60°) and melts at 159° to 160°. It is readily soluble in cold ether, benzene, chloroform, and acetic acid, and almost insoluble in hot ligroin.

	Calculated for $C_{25}H_{20}O_2$.	Found.
C	85.24	85.17
H	5.68	5.93

This phenol reacts vigorously at the ordinary temperature with cold concentrated nitric acid and yields nitro derivatives. These nitro bodies will be investigated later.

III. *Addition of Benzoin to Piperonyleneacetone.*

3,4-Diphenyl-5-piperyl-4-oxy-Δ_2-keto-R-hexene,

$$CH.C_6H_3.(CH_2O_2)$$

$C_6H_5.C.(OH)$ ... CH_2

.—One molecule (6 grams)

$C_6H_5.C.$ ... CO

$$CH$$
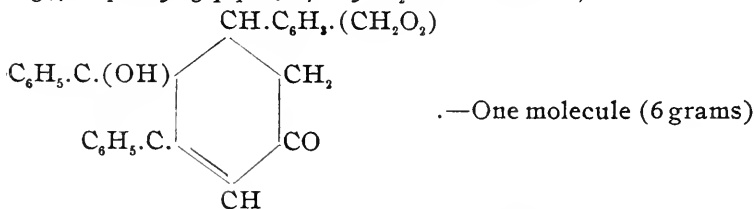
of benzoin and 1 molecule of piperonyleneacetone are dis-

solved in hot absolute ethyl alcohol (100 cc.) and a solution (4 cc.) of sodium ethylate (0.5 gram sodium in 30 cc. absolute alcohol) is added. As in all these condensation-reactions with sodium ethylate, this mixture assumes a deep red coloration. Upon standing for two hours, rosettes of yellow, needle-like crystals separate. These crystals, upon recrystallization from glacial acetic acid, are obtained in fine, white, glittering needles, melting at 240°. The substance is soluble in hot chloroform ; sparingly soluble in hot benzene and alcohol ; and insoluble in ether and ligroin (40° to 60°).

	Calculated for $C_{25}H_{20}O_4$.	Found.
C	78.12	78.00
H	5.21	5.35

The method above described for the preparation of 3,4-diphenyl-5-piperyl-4-oxy-Δ_2-keto-R-hexene does not progress as smoothly and as completely as when 1 molecule each of piperonal (4.25 grams) and of pure acetone (1.7 grams) is used in place of the piperonyleneacetone, and the reaction is carried out at the temperature of the water-bath. The crystals obtained by this method are very pure and clean, and the yield is almost quantitative, especially if the mother-liquor is treated again with more sodium ethylate and the mixture again boiled.

Ten per cent sodium hydroxide solution also effects the condensation. However, the yield is poor.

Oxime of 3,4-Diphenyl-5-piperyl-4-oxy-Δ_2-keto-R-hexene.— This oxime is prepared in an analogous method to that described previously for the preparation of oximes. When recrystallized from a mixture of alcohol and ligroin, crystals are formed melting at 190° to 191°. It is soluble in hot alcohol, cold ether, chloroform, and hot benzene, and is insoluble in ligroin (40° to 60°).

	Calculated for $C_{25}H_{21}O_4N$.	Found.
N	3.51	3.78

IV. Addition of Cuminoin to Benzalacetone.[1]

3,4-Dicumyl-5-phenyl-4-oxy-Δ_2-keto-R-hexene,

$$CH.C_6H_5$$

$(CH_3)_2CH.C_6H_4.C.(OH)$ ⟨ ⟩ CH_2

$(CH_3)_2.CH.C_6H_4.C$ ⟨ ⟩ CO .—Cuminoin, in general,

$$CH$$
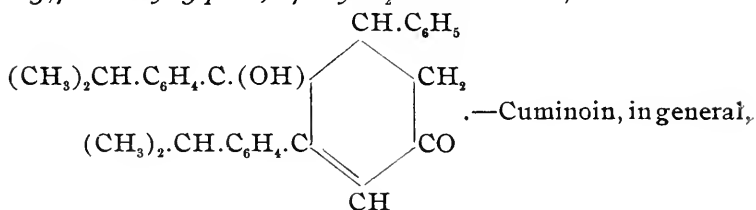
reacts less rapidly than benzoin, and the yields of Δ_2-keto-R-hexene derivatives are poorer.

One molecule (6 grams) of pure cuminoin[2] and 1 molecule (3 grams) of pure benzalacetone dissolved in hot absolute ethyl alcohol (60 cc.) are treated with a solution (6 cc.) of sodium ethylate (0.5 gram sodium in 30 cc. absolute alcohol). Upon the addition of the sodium ethylate, the mixture turns deep red, and, after standing for six hours, clusters of needles separate. By recrystallizing twice from glacial acetic acid, pure 3,4-dicumyl-5-phenyl-4-oxy-Δ_2-keto-R-hexene is obtained. It melts at 214°. It is soluble in cold acetic ether, chloroform, hot benzene, and ligroin (110° to 120°); insoluble in cold alcohol, ligroin (40° to 60°), and ether. The yield is about 27 per cent of the theoretical.

	Calculated for $C_{30}H_{32}O$.	Found.
C	84.90	84.77
H	7.54	7.83

Oxime of the 3,4-Dicumyl-5-phenyl-4-oxy-Δ_2-keto-R-hexene.— A molecule of the substance dissolved in alcohol was boiled with 3 molecules of hydroxylamine hydrochloride for an hour. On cooling, nothing appeared, but after the larger portion of the alcohol had been distilled off in the water-bath a solid separated, which, on being well washed with water and recrystallized from a mixture of benzene and ligroin (40° to 60°), gave fine, white needles melting at 208°. It may be recrystallized also from aqueous alcohol. The analysis shows it to be the monoxime.

[1] Dissertation, Chicago, 1897, p. 19.
[2] Ber. d. chem. Ges., **26**, 64.

	Calculated for $C_{20}H_{23}O_2N$.	Found.
N	3.11	3.30

The substance is easily soluble in cold acetic acid, benzene, and acetic ether; insoluble in ligroin (40° to 60°).

3,4-Dicumyl-5-phenylphenol Acetate.—The body can easily be prepared by boiling the Δ_2-keto-R-hexene derivative with a mixture of acetic anhydride and anhydrous sodium acetate for forty-five minutes, or until the mixture becomes decidedly pink in color. The solution is then poured into a large amount of cold water and allowed to settle. After recrystallization from glacial acetic acid it is obtained in large bunches of long, radiating fibers, and melts, when pure, at 122°. It is soluble in cold benzene, chloroform, ether, and ligroin (40° to 60°), in hot alcohol and acetic acid.

	Calculated for $C_{32}H_{32}O_2$.	Found.
C	85.71	85.60
H	7.14	7.55

The acetyl derivative, when hydrolyzed by means of alcoholic potash, yields 3,4-dicumyl-5-phenylphenol.

By warming the acetate in a water-bath for ten minutes with four molecules of alcoholic potash and pouring into dilute hydrochloric acid, an amorphous mass is obtained which crystallizes from warm alcohol in large thin plates, melting at 137°. This substance is soluble in cold acetic ether, benzene, chloroform, ether, and hot ligroin (40° to 60°); insoluble in caustic soda.

	Calculated for $C_{30}H_{30}O$.	Found.
C	88.66	88.26
H	7.39	7.99

The addition-reactions of cuminoin with cuminalacetone, piperonyleneacetone, and anisylideneacetone are being studied at present, and I hope to be able soon to publish the results obtained.

V. *Addition of Anisoin to Benzalacetone.*

3,4-Dianisyl-5-phenyl-4-oxy-Δ_2-keto-R-hexene,

$$CH_3O.C_6H_4.C.(OH) \overset{CH.C_6H_5}{\underset{CH}{\bigcirc}} \begin{matrix} CH_2 \\ CO \end{matrix}$$

CH$_3$O.C$_6$H$_4$.C

.—Anisoin adds itself to the
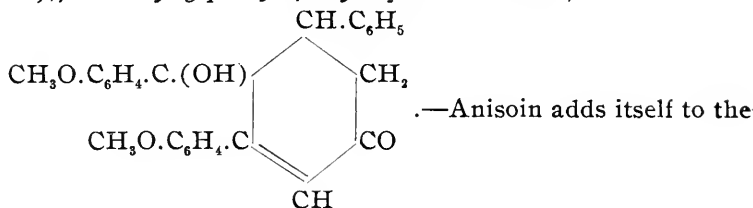
ethylene grouping much more readily than either cuminoin or benzoin to yield the expected 1,5-diketone, but the readiness with which this 1,5-diketone loses water to form the corresponding Δ_2-ketone-R-hexene derivative is markedly less. In fact, the 1,5-diketone constitutes the major portion of the reaction-product. Attempts to prepare the 1,5-diketone pure, *i. e.*, free from the Δ_2-keto-R-hexene derivatives, have failed partially. However, its approximate melting-point has been obtained, namely, 168° to 174°. When boiled with the ordinary solvents in which it is soluble, the 1,5-diketone loses water and forms the Δ_2-keto-R-hexene derivative, which melts at 207°.

The mixture of the 1,5-diketone and the Δ_2-keto-R-hexene derivative is prepared as follows :

One molecule (4.4 grams) of anisoin and 1 molecule (2.38 grams) of benzalacetone are dissolved in absolute ethyl alcohol (62 cc.) and to the mixture sodium ethylate solution (4 cc.) is added. The solution becomes deep red, and upon standing for two hours deposits a large mass of crystals (2.4 grams). The solid is filtered off and washed well with absolute alcohol. A trial determination of the melting-point shows that the product is a mixture. It melts at 168° to 174° and 204°. The mother-liquor from the crystals, upon treatment with more sodium ethylate solution yields more of the same products (0.4 gram). Upon recrystallization from either of three solvents—benzene, alcohol, or acetic acid—fine, white, needle-like crystals are obtained, having a constant melting-point of 207°. It is soluble in chloroform, slightly soluble in ligroin, and insoluble in ether.

	Calculated for $C_{26}H_{24}O_4$.	Found.
C	78.00	77.62
H	6.00	6.13

The acetate and oxime have been prepared, but as yet no analyses have been made, but the physical properties determined correspond very closely with those of the other Δ_2-keto-R-hexene derivatives which I have prepared.

An investigation of the reaction of anisoin with cuminalacetone, piperonyleneacetone, and anisylideneacetone is being carried on.

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A NEW METHOD FOR THE DETERMINATION OF FREE LIME AND ON SO-CALLED "DEAD BURNT" LIME.

BY EDWARD H. KEISER AND S. W. FORDER.

A great many attempts have been made to devise a quantitative method for the determination of free lime in Portland cements, basic phosphate slags, commercial quicklime, and similar substances, but none of the methods thus far proposed has been satisfactory, nor have any of them come into general use. The difficulty is that in the substances mentioned, besides the free lime, there are basic lime compounds, such as the basic di- and tricalcium silicates which are decomposed by water with the formation of calcium hydroxide. When these substances are treated with aqueous solutions, as for example, sugar solution, for the purpose of dissolving the free lime, the water of the solution at once acts upon the basic lime compounds and forms calcium hydroxide. It is, therefore, impossible to determine how much of the lime that is found was in combination and how much was in free condition.

The method described below depends upon the fact that uncombined lime, that is, free lime, combines almost instantly with water, whereas the basic calcium silicates are acted upon much more slowly by water. The process is carried out as

follows : A weighed quantity of the substance, 0.2 to 0.5 gram, is first heated in a platinum crucible to drive off moisture, or in the case of cements, is heated with the blast-lamp for a few minutes to expel any carbon dioxide, and after cooling in a desiccator is again weighed. A few drops of distilled water, which has been recently boiled, are then added and the crucible placed in the brass protector, D, shown in the figure. (D is simply a cylindrical box provided with a screw-top carrying a brass inlet and outlet tube. The thread of the cap is made air-tight with a little white lead and oil.) The protector is put into the air-bath and the temperature is raised to 85° C. and allowed to remain at about this point for thirty minutes. Then a slow current of air is drawn through the apparatus and the temperature raised to 185°. The air is freed from carbon dioxide and moisture by passing through the potash bulb and calcium chloride tube, A and B., as shown in the figure. After drying in this way for thirty minutes the apparatus is disconnected, the protector removed from the air-bath, and the crucible taken out and placed in a desiccator, and when cold is weighed. The increase of weight is the weight of water taken up by the quicklime to form calcium hydroxide.

The method and apparatus were first tested by hydrating pure lime obtained by the ignition of Iceland spar. A weighed quantity of Iceland spar was heated for from five to ten minutes in a platinum crucible with the blast-lamp. After cooling in a desiccator the weight of quicklime was determined. The hydration was then carried out as above described. The following results were obtained :

Weight of lime taken. Gram.	Weight of water absorbed. Gram.	Weight of lime found. Gram.	Lime found. Per cent.
0.2239	0.0724	0.2252	100.60
0.3287	0.1049	0.3263	99.26
0.2368	0.0757	0.2355	99.45
0.2799	0.0909	0.2828	101.00
0.5322	0.1704	0.5300	99.60
0.1579	0.0507	0.1577	99.90
0.1810	0.0581	0.1807	99.88
0.2425	0.0852	0.2433	100.30
0.2487	0.0794	0.2470	99.33

A = KOH Bulb
B = CaCl₂ Tube
C = Thermometer
D = Brass Protector
E = Porcelain dish for crucible
F = Platinum crucible
G = Copper air bath
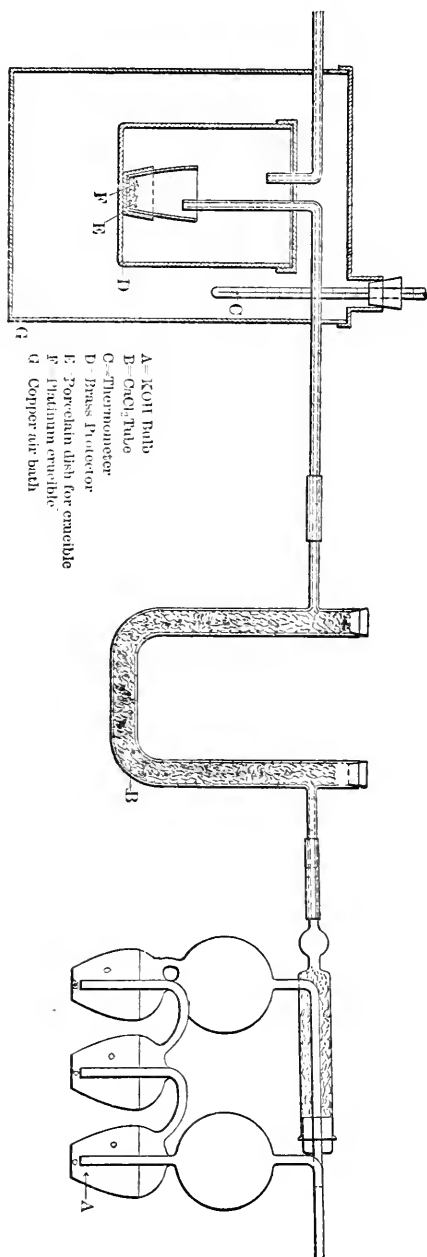
These results show that the method is quantitative and that lime that has been heated to the highest temperature attainable in a platinum crucible with the blast-lamp is completely slaked in twenty minutes at 85°. In fact, in the case of pure quicklime, the slaking is very rapid. The calcium hydroxide was found to be constant in weight up to 250°, beyond which it was not tested. The calcium hydroxide, when exposed to the air, of course, takes up carbon dioxide. It is, therefore, necessary to keep the crucible in a desiccator containing caustic potash instead of calcium chloride, and to weigh as rapidly as possible.

Hydration of Commercial Lime.

For the determination of calcium oxide in commercial quicklime a large piece was taken and the exterior portions broken away and a sample for analysis taken from the interior of the lump. This was quickly placed in a tightly stoppered weighing-tube. Portions of this were weighed off in a platinum crucible and then water was added in a little greater quantity than was necessary for slaking, the crucible put in the protector, warmed to 85° for some minutes, and then a slow current of air free from carbon dioxide drawn through for half an hour, the temperature now being raised to 185°. After cooling in the desiccator, the increase in weight was determined and from this the percentage of lime in the sample calculated. The following results were thus obtained :

Percentage of water.	Percentage of calcium oxide calculated.
29.11	90.56
29.21	90.88
28.98	90.20

This same specimen of quicklime, after ignition over the blast-lamp and immediate hydration, gave the following :

Water taken up. Per cent.	Lime by calculation. Per cent.
32.30	100.50
32.36	100.70

This shows the extent to which the lime had been acted upon by the moisture and carbon dioxide of the air.

The method is also well adapted for rapidly determining the value of limestones for the purpose of making quicklime. Thus a small quantity of the limestone is weighed in a platinum crucible, then ignited with the blast-lamp, and, after weighing, the quicklime is hydrated by this method. From the weight of water taken up the per cent of lime is calculated. The first series of determinations given above shows what results would be obtained with a pure limestone, such as Iceland spar or calcite. The following determinations were made with a siliceous dolomite from Arkansas.

Weight of dolomite. Gram.	Weight of water taken up. Gram.	Percentage of lime.
0.2974	0.0137	14.33
0.2896	0.0134	14.40

Hydration of Dead Burnt Lime.

It is generally believed by practical men that lime that has been very highly heated becomes dead burnt or inert to water. Statements to this effect are found in chemical literature. Thus Dammer[1] states that " very high temperatures must be avoided in the preparation of lime, especially if impure calcium carbonate is used, because the lime at too high temperatures becomes dead burnt, that is. it becomes incapable of uniting with water.'' Zulkowski[2] maintains that a portion of the lime in Portland cements is in this dead burnt condition. In an article in the Thonindustrie Zeitung, 1902, the same author suggests the formula Ca$\left\langle\begin{smallmatrix}O\\O\end{smallmatrix}\right\rangle$Ca for dead burnt lime.

For the purpose of determining the behavior of highly heated lime towards water, powdered Iceland spar was placed between the carbon pencils of an electric arc and the current passed for one hour. A number of particles of semi-fused lime were thus obtained. These particles were carefully separated from the powder that had not melted and weighed quantities were hydrated by the above described method. It was found that this lime that had been heated in the electric arc

[1] Handbuch der anorganischen Chemie, II., 2, 294.
[2] Chemische Industrie, 1901, p. 290.

slaked more slowly than that which had not been heated to
so high a temperature, but still it combined slowly with water
at ordinary temperatures, and on allowing it to stand with
water at the ordinary temperature for twenty-four hours it
had slaked completely.   When the temperature was raised to
85° the slaking was complete in two hours.   The following
results were obtained :

Weight of lime taken. Gram.	Weight of water taken up. Gram.	Lime calculated from water. Per cent.
0.2799	0.0909	101.0
0.2050	0.0661	100.3
0.5322	0.1704	99.6
0.3909	0.1279	101.0

Another specimen of lime that had been heated with the
oxy-coal-gas blow-pipe gave the following result :

Weight of lime. Gram.	Weight of water taken up. Gram.	Percentage of lime.
0.3557	0.1163	100.5

These experiments show that pure lime that has been
heated to very high temperatures, even semi-fused lime, is not
inert to water and that it slakes comparatively rapidly if the
water is warm.   That the slaking with cold water is slower
than in the case of ordinary lime may be due to the fact that
lime that has been heated to very high temperatures is much
more compact and less porous than the ordinary lime.   The
surface exposed to the action of water being much less the
time required for slaking would necessarily be greater.   We
see from these experiments that pure lime cannot be made
inert to water by heating to high temperatures.   The inert-
ness of commercial lime is probably due to the presence of
compounds of silica and iron oxide with the lime which are
decomposed very slowly by the water.

Hydration of Calcium Silicates.

The hydration of lime and its compounds was further
studied by making synthetically the compounds that are as-
sumed to be present in Portland cement, and then hydrating
these substances by this method.   Pure lime and silica were

mixed in molecular quantities so as to give, when fused, the compounds, CaO, SiO_2, $2(CaO)SiO_2$, $2\frac{1}{2}(CaO)SiO_2$, $3(CaO)SiO_2$, and $4(CaO)SiO_2$. The lime was obtained by the ignition of pure precipitated calcium carbonate. The silica was prepared by conducting silicon tetrafluoride into water and then drying and igniting the gelatinous silicic acid thus formed. Intimate mixtures of lime and silica in the proportions to form the above compounds were heated by projecting vertically the flame of the oxy-coal-gas blowpipe down upon the mixtures in a cavity made in a fire-brick. The heat thus obtained was sufficient to melt all except the last mixture, namely, the $4(CaO)SiO_2$. The fused masses were in each case carefully separated from the unfused portions, they were chilled by sprinkling with cold water, dried, and preserved in stoppered bottles. Weighed quantities were then hydrated by this method. The hydraulic properties of each compound were also examined by mixing some of the powdered compound with water and observing whether the mass set and became hard. The following table contains the results that were obtained :

Compound.	Hydraulic properties.	Weight taken.	Weight of water taken up.	Percentage of water.	Percentage of lime.
		Gram.	Gram.		
CaO, SiO_2	None	0.4829	0.0004	0.082	0.26
$2(CaO)SiO_2$	Not quite as hard as cement	0.3988	0.0017	0.42	1.33
"	Not quite as hard as cement	0.3997	0.0012	0.30	0.93
$2\frac{1}{2}(CaO)SiO_2$	Not quite as hard as cement	0.4241	0.0022	0.52	1.61
$3(CaO)SiO_2$	Hard as cement	0.4341	0.0044	1.01	3.15
$4(CaO)SiO_2$	None	0.4241	0.0262	6.15	19.15

We conclude from these results that lime in combination with silica in quantities not exceeding 3 molecules of lime for 1 molecule of silica is only slowly acted upon by water and that this method of determining lime can be used to deter-

mine free lime in the presence of the basic di- and tricalcium silicates that are assumed to be present in Portland cements.

Hydration of Calcium Aluminates.

The mono-, di-, and tricalcium aluminates were also prepared synthetically by fusing molecular quantities of pure alumina and lime with the oxy-coal-gas blowpipe flame. The alumina was prepared by heating the hydroxide that had been obtained by precipitation from the chloride with ammonia. The aluminates all fused much more easily than the silicates under the oxy-coal-gas blowpipe. Weighed quantities were hydrated by our method as in the case of the silicates and the hydraulic properties were also noted. It was found that the aluminates differ markedly from the silicates in their behavior towards water. This is shown by the following results :

Compound.	Hydraulic properties.	Weight taken.	Weight of water taken up.	Percentage of water.	Percentage of lime.
		Gram.	Gram.		
$(CaO)Al_2O_3$	Set very hard	0.4886	0.0653	13.34	41.52
$2(CaO)Al_2O_3$	Like a cement	0.4543	0.0716	15.76	49.04
$3(CaO)Al_2O_3$	None	0.4072	0.0796	19.55	60.80

We see from this that the aluminates are hydrated very much more rapidly than the silicates, in fact they behave like free lime when warmed with water to $85°$ for thirty minutes. In the case of the monocalcium aluminate the percentage of water taken up shows a hydration of the alumina as well as of the lime. It is our intention to make a further study of this part of the subject. In determining free lime, therefore, by this method in substances containing calcium aluminates, this fact must be borne in mind, and the lime in combination with the alumina must be deducted from the total lime found.

Behavior of Cements.

As in commercial cements the proportion of alumina usually varies from 5 to 9 per cent, we have prepared several cements

by fusing with the oxy-coal-gas blowpipe pure alumina, lime, and silica in definite proportions and have then hydrated the resulting cements by our method. The following results were obtained :

Composition of cement.		Hydraulic properties.	Water taken up. Per cent.
5 per cent	Al$_2$O$_3$	Set slowly, did not become	
25 "	SiO$_3$	quite as hard as Portland	
70 "	CaO	cement	1.43
9 "	Al$_2$O$_3$	Set slowly and became	
21 "	SiO$_3$	quite as hard as Portland	
70 "	CaO	cement	2.16
15 "	Al$_2$O$_3$		
15 "	SiO$_2$	Set slowly and became very	
70 "	CaO	hard	4.65

We see from this that as the proportion of alumina increases the percentage of water taken up increases, but if the proportion of alumina does not exceed 10 per cent, as is the rule in commercial cements, then the amount of water taken up does not exceed 3 per cent.

A number of the best known varieties of commercial cements were then examined by our method. In each case the sample was weighed in a platinum crucible, then ignited for a few minutes over the blast-lamp, and after cooling in the desiccator it was weighed. The cement was then moistened with a few drops of water, the crucible put into the protector and warmed to 85° for thirty minutes. Then the temperature was raised to 185° and a slow current of air drawn through until constant weight was obtained. The following results were obtained :

Cement.	Water taken up. Per cent.	Cement.	Water taken up. Per cent.
A	1.16	I	1.81
B	1.97	J	2.99
C	2.09	K	2.77
D	2.67	L	2.18
E	2.88	M	2.61
F	2.66	N	2.64
G	3.01	O	3.04
H	3.10		

These cements all had good, "sound" tests, and in nearly all cases less than 3 per cent of water was taken up. We conclude from this and from the preceding experiments upon cements that this water was taken up by the aluminates and that little or no free lime was contained in these cements. One variety of Portland cement that we examined gave 10.17 per cent of water taken up. We concluded that 7 per cent of this must be due to free lime being present. Our conclusion was justified, for, on making a pat of the neat cement and allowing it to set thoroughly, it was immersed in boiling water, and on removal from the water it showed signs of cracks and had become quite soft and readily disintegrated.

Two varieties of natural cements were tested and gave the following values :

Natural cement.	Water taken up. Per cent.
A	5.76
B	3.70

Finally, we have tested our method by adding weighed amounts of pure lime to a cement of known behavior and then, after ignition with the blast-lamp, have again determined the percentage of water taken up. Thus, cement A, which took up 1.16 per cent of water, had 15.40 per cent of lime added to it. Then, on retesting, it took up 6.25 per cent of water. Percentage of lime corresponding to 1.16 per cent of water, equals 3.60. This, plus the 15.40 per cent added, equals 19.00 per cent. Lime, corresponding to 6.25 per cent of water, equals 19.44.

We conclude from our experiments that if a Portland cement, containing less than 10 per cent of alumina, takes up more than 3 per cent of water, then this excess is due to the free lime present.

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ST. LOUIS, Oct., 1903.

SOME ADDITION-REACTIONS OF SULPHINIC ACIDS.

BY ELMER P. KOHLER AND MARIE REIMER.

Only two cases of direct union between sulphinic acids and other substances have, so far as we know, been described. Hinsberg[1] found that sulphinic acids combine with quinones and with substances that have a quinoid structure :

$$C_6H_4O_2 + C_6H_5SO_2H = C_6H_4(OH)_2SO_2C_6H_5.$$
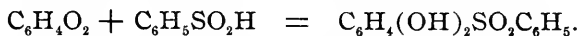
Hantsch and Glogauer[2] described sulphonehydrazo compounds which they obtained by direct union between benzenesulphinic acid, and azo and diazo compounds.

We have found that sulphinic acids combine more or less readily with aldehydes, Δ-1,2-unsaturated acids, and Δ-1,2-unsaturated ketones. We did not succeed in getting addition-products with saturated ketones.
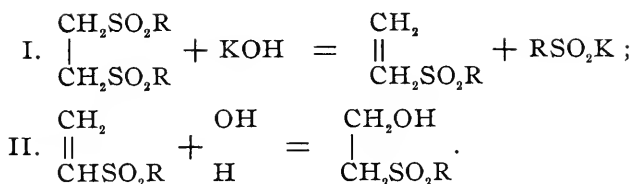
The 1,1-oxysulphones obtained by the union of aldehydes and sulphinic acids are very unstable substances. Unless derived from non-volatile aldehydes, they slowly change in the air, even when they are perfectly pure and dry, the aldehyde evaporating while the sulphinic acid undergoes oxidation. In solution, all rapidly dissociate into their components, hence they can be kept only in the presence of a considerable excess of one of the constituents. This explains why these substances cannot be obtained by the action of alkalies on the halogen substitution-products of sulphones.[3]

When a sulphinic acid combines with an α,β-unsaturated acid or an α,β-unsaturated ketone the sulphone group invariably goes into the β-position. The resulting products are stable substances which crystallize well and which can be used for identifying minute quantities of unsaturated ketones. They are very sensitive to alkalies, which smoothly split off the sulphinic acid and regenerate the unsaturated compound. This behavior may explain the fact that only 1,2-disulphones are easily hydrolyzed by alkalies. The hydrolysis is probably the result of two successive processes :

[1] Ber. d. chem. Ges., **27**, 3259.

[2] *Ibid.*, **30**, 2548.

[3] Fromm : Ann. Chem. (Liebig), **253**, 135.

$$\text{I. } \begin{array}{c} CH_2SO_2R \\ | \\ CH_2SO_2R \end{array} + KOH = \begin{array}{c} CH_2 \\ || \\ CH_2SO_2R \end{array} + RSO_2K ;$$

$$\text{II. } \begin{array}{c} CH_2 \\ || \\ CHSO_2R \end{array} + \begin{array}{c} OH \\ \\ H \end{array} = \begin{array}{c} CH_2OH \\ | \\ CH_2SO_2R \end{array}.$$

Ketones that have two double linkages in the α,β-position combine in the cold, with one molecule of a sulphinic acid. The resulting unsaturated sulphones combine with bromine, but all efforts to add a second molecule of a sulphinic acid were fruitless.

The ease with which sulphinic acids combine with unsaturated ketones and the stability of the resulting sulphones led us to study some ketones which contain the grouping that Thiele has called "a conjugated system of vicinal double unions."[1] We found that these ketones combine, in the cold, with 1 molecule of a sulphinic acid, and that the addition takes place at the double linkage nearest the carbonyl group, the sulphone group going into the β-position.
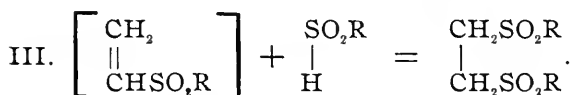
The study of sulphinic acids has led to the discovery of certain peculiar reactions for which no satisfactory explanation has been offered. Otto[2] found, for example, that unsymmetrical dihalogen derivatives of aliphatic hydrocarbons give symmetrical disulphones when heated with sulphinates.

$$CH_3CHBr_2 + 2RSO_2Na = \begin{array}{c} CH_2SO_2R \\ | \\ CH_2SO_2R \end{array} + 2NaBr.$$
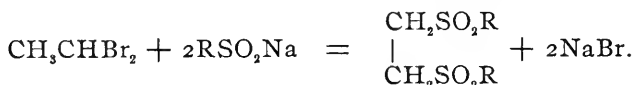
He explains this result by assuming a molecular rearrangement, an assumption for which there is no experimental evidence and which is improbable in view of the well-known stability of unsymmetrical disulphones. The discovery that sulphinic acids combine with unsaturated compounds suggests a different explanation, which does not involve molecular rearrangement.

[1] Ann. Chem. (Liebig), 306, 53.
[2] J. prakt. Chem., [2], 40, 505.

$$\text{I.} \quad \begin{matrix} CH_3 \\ | \\ CHBr_2 \end{matrix} + RSO_2Na = \begin{matrix} CH_3 \\ | \\ CHBrSO_2Na \end{matrix} + NaBr;$$

$$\text{II.} \quad \begin{matrix} CH_3 \\ | \\ CHBrSO_2Na \end{matrix} + RSO_2Na =$$

$$\begin{matrix} CH_2 \\ || \\ CHSO_2Na \end{matrix} + RSO_2H + NaBr;$$

$$\text{III.} \quad \begin{bmatrix} CH_2 \\ || \\ CHSO_2R \end{bmatrix} + \begin{matrix} SO_2R \\ | \\ H \end{matrix} = \begin{matrix} CH_2SO_2R \\ | \\ CH_2SO_2R \end{matrix}.$$
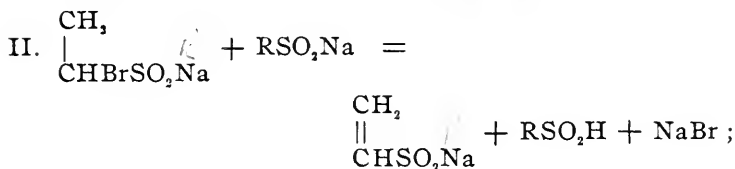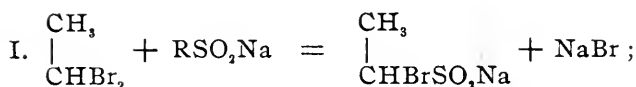
We tried to isolate the hypothetical unsaturated sulphone (included in brackets) but failed. We obtained the halogen sulphone and found that when it is heated with a sulphinate most of the latter is transformed into the corresponding " disulphoxide." Since these disulphoxides are very easily obtained from sulphinic acids and not from sulphinates, this result indicates that at some stage of the process sulphinic acid is liberated as required by the above explanation.

I. Addition of Paratoluenesulphinic Acid to Aliphatic Aldehydes.

Paratoluenesulphinic acid dissolves in liquid aliphatic aldehydes with considerable evolution of heat. The addition-products which separate from this solution on cooling generally contain considerable quantities of unchanged sulphinic acid. They may be purified by repeated solution in ether and precipitation with ligroin, but pure products are more easily obtained by allowing the reaction to take place in ethereal solution. The method of procedure used in the preparation and purification of the substances described below, was as follows : A considerable excess of the aldehyde was added to an ethereal solution of the acid and the mixture boiled for half an hour. The liquid was then cooled in ice-water and ligroin added until precipitation just commenced. The crystalline precipitate which separated was redissolved in ether which contained a small quantity of the aldehyde and

again precipitated with ligroin. This process was repeated until the product was free from acid. Then the substance was dried rapidly in a current of air and analyzed at once.

1. Addition to Acetaldehyde : 1-Paratolylsulphonethanol(1),

$$CH_3CH{\Large\langle}{}^{OH}_{SO_2C_7H_7}$$.—The compound crystallizes in thick

plates, which may be kept in ether and ligroin containing a small quantity of acetaldehyde. When dry, it loses aldehyde slowly in the cold, rapidly on heating. For this reason it does not melt sharply. It begins to soften at 52° and is liquid at 72°.

I. 0.2291 gram substance gave 0.4531 gram CO_2 and 0.1261 gram H_2O.

II. 0.2254 gram substance gave 0.4442 gram CO_2.

III. 0.2089 gram substance gave 0.2692 gram $BaSO_4$.

	Calculated for $C_9H_{12}SO_3$.	I.	Found. II.	III.
C	54.00	53.94	53.73	....
H	6.00	6.11	....	....
S	16.00	....	....	16.5

2. Addition to Isobutyric Aldehyde : 1-Paratolylsulphone-3-

methylpropanol(1), $${}^{CH_3}_{CH_3}{\Large\rangle}CH.CH{\Large\langle}{}^{OH}_{SO_2C_7H_7}$$.—The substance

crystallizes from ether in colorless needles ; from ether and ligroin in thick plates. It slowly decomposes in the air. An analysis gave the following result :

0.2020 gram substance gave 0.4277 gram CO_2 and 0.1290 gram H_2O.

	Calculated for $C_{11}H_{16}SO_3$.	Found.
C	57.90	57.67
H	7.02	7.09

3. Addition to Heptoic Aldehyde : 1-Paratolylsulphonehep-

tanol(1), $CH_3(CH_2)_5CH{\Large\langle}{}^{OH}_{SO_2C_7H_7}$.—This product is less sol-

uble in ether than the substances previously described, hence it was possible to purify it by dissolving it in boiling anhy-

drous ether and cooling the solution in ice-water.   It crystallizes in fine, white needles, which decompose on heating.   It is insoluble in water and ligroin ; readily soluble in ether, alcohol, acetone, benzene, and chloroform.   It loses aldehyde on exposure to the air.

I. 0.1932 gram substance gave 0.4361 gram CO_2 and 0.1386 gram H_2O.

II. 0.2224 gram substance gave 0.5020 gram CO_2 and 0.1608 gram H_2O.

	Calculated for $C_{14}H_{22}SO_3$.	I.	II.
C	52.22	61.56	61.55
H	8.15	7.97	8.03

II. Addition of Paratoluenesulphinic Acid to Aromatic Aldehydes.

Paratoluenesulphinic acid combines with aromatic aldehydes under the same conditions as those under which it combines with aliphatic aldehydes.   The compound with benzaldehyde was not obtained in pure condition.   The compounds with metanitrobenzaldehyde and paranitrobenzaldehyde, however, are much more stable than the corresponding compounds with aliphatic aldehydes.   They do not change in the air, and they can be recrystallized from alcohol, acetone, and other organic solvents.

1. Addition to Metanitrobenzaldehyde : 1-Paratolylsulphone-1-metanitrophenylmethanol, $m\text{-}NO_2C_6H_4CH\begin{smallmatrix}OH\\SO_2C_7H_7\end{smallmatrix}$.—Ethereal solutions of the aldehyde and the acid were mixed and warmed on the water-bath.   After a few minutes the product separated in fine, white needles, that melt to a yellow liquid at 110°.

0.2860 gram substance gave 0.5738 gram CO_2 and 0.1139 gram H_2O.

	Calculated for $C_{14}H_{13}NSO_5$.	Found.
C	54.72	54.71
H	4.23	4.43

The substance is readily soluble in alcohol and acetone, slightly soluble in ether. It is decomposed by boiling water, which dissolves the acid and leaves most of the aldehyde. A solution of sodium carbonate decomposes it slowly in the cold.

   2. Addition to Paranitrobenzaldehyde : 1-Paratolylsulphone-1-paranitromethanol, $p\text{-}NO_2C_6H_4CH\begin{subarray}{l} \diagup OH \\ \diagdown SO_2C_7H_7 \end{subarray}$. – The addition was carried out in ethereal solution and the product recrystallized from acetone.

   0.2028 gram substance gave 0.4070 gram CO_2 and 0.0786 gram H_2O.

	Calculated for $C_{14}H_{13}NSO_5$.	Found.
C	54.72	54.73
H	4.23	4.08

The substance crystallizes in pale-yellow needles, melting at 116°. It is soluble in alcohol and acetone, slightly soluble in ether, insoluble in ligroin and water.

   While this work was in progress Meyer[1] described a sub-stance which he obtained by the direct union of paratoluene-sulphinic acid and formaldehyde. By treating this substance —paratolylsulphonecarbinol—with acetic anhydride, Meyer obtained an acetyl derivative, and by treating it with aniline he obtained an anilide. Since the product obtained from paranitrobenzaldehyde is more stable than the corresponding aliphatic compounds, we expected it to give similar products with these reagents. This is not the case. The substance dissolves completely in cold acetic anhydride, and when this solution is allowed to evaporate the acetal of paranitrobenzaldehyde separates in beautiful, needle-shaped crystals that melt at 126°.5.

   0.1977 gram substance gave 0.8771 gram CO_2 and 0.0784 gram H_2O.

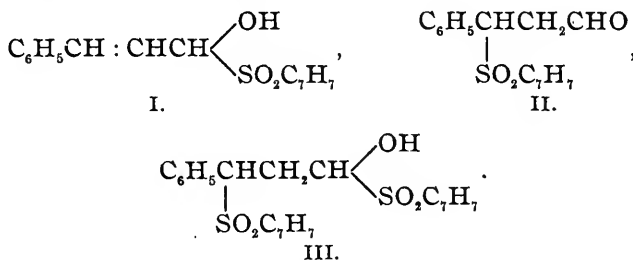|	Calculated for $NO_2C_6H_4CH\begin{subarray}{l} \diagup OCOCH_3 \\ \diagdown OCOCH_3 \end{subarray}$.	Found.
C	52.17	52.01
H	4.35	4.40

[1] J. prakt. Chem., [2], **63**, 167.

The acetal is formed from the oxysulphone much more easily than from the aldehyde itself, since no acetal was obtained when a solution of the aldehyde in acetic anhydride was boiled with an inverted condenser or heated in a sealed tube to 150°. A fair yield of the acetal was obtained, however, by boiling a solution of the aldehyde in acetic anhydride, to which a small quantity of concentrated sulphuric acid had been added.

To test the action of aniline on the oxysulphone a small quantity of the substance was added to a boiling solution of aniline in ether. The substance dissolved and fine, white needles separated from the hot solution. These were very soluble in water and alcohol, insoluble in ether. They melted at 121° to 122°. Since the same substance was obtained by treating paratoluenesulphinic acid with aniline in ethereal solution, it must be the aniline salt of paratoluenesulphinic acid. This shows that the oxysulphone is easily decomposed by aniline.

III. Addition of Paratoluenesulphinic Acid to Cinnamic Aldehyde.

Cinnamic aldehyde combines with acid sulphites to form three different substances. The corresponding addition-products with paratoluenesulphinic acid would be represented by the following formulas:

$$C_6H_5CH:CHCH \begin{cases} OH \\ SO_2C_7H_7 \end{cases}, \qquad \begin{array}{c} C_6H_5CHCH_2CHO \\ | \\ SO_2C_7H_7 \end{array},$$
$$\text{I.} \qquad\qquad\qquad\qquad \text{II.}$$

$$\begin{array}{c} C_6H_5CHCH_2CH \\ | \\ SO_2C_7H_7 \end{array} \begin{cases} OH \\ SO_2C_7H_7 \end{cases}.$$
$$\text{III.}$$

Only two of these substances were obtained; the monosulphone represented by II. and the disulphone represented by III. Whether the monosulphone or disulphone be formed in any given experiment depends partly upon the conditions and

partly upon the relative amounts of the substances. When the acid is dissolved in the aldehyde, and when the two are brought together in ethereal solution, the product is the disulphone, even when the aldehyde is present in large excess. This result is due to the difference in the solubility of the monosulphone and the disulphone in these media. In water and in alcohol, where there is no such difference, the result depends upon the relative amounts of acid and aldehyde that are brought together.

The *monosulphone* crystallizes in white, globular aggregates that melt at 78°. It is readily soluble in alcohol, ether, and benzene, insoluble in water and ligroin. An analysis gave the following results :

0.2285 gram substance gave 0.5580 gram CO_2 and 0.1101 gram H_2O.

	Calculated for $C_{16}H_{16}SO_3$.	Found.
C	66.66	66.59
H	5.55	5.35

That the substance has the structure (II.) assigned to it is shown by the following experiments :

1. An ethereal solution of the substance was shaken with an aqueous solution of acid potassium sulphite. A crystalline compound separated at once. When this was treated with dilute alkalies the original substance was regenerated. This result proves the presence of the aldehyde group.

2. The substance was oxidized by warming it with dilute nitric acid (1 : 3) on the water-bath. An acid separated from the solution, on cooling, in fine, white needles, melting at 196° to 197°. This same acid was obtained by adding paratoluenesulphinic acid to cinnamic acid, and it will be shown below that its structure is represented by the formula

$$C_6H_5CHCH_2CO_2H$$
$$|$$
$$SO_2C_7H_7$$
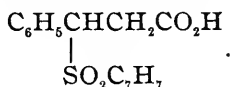
This proves that the sulphone group is in the β-position with reference to the aldehyde group.

The disulphone (III.) is obtained by treating either the

aldehyde or the monosulphone with paratoluenesulphinic acid in ethereal solution. It is soluble in benzene, alcohol, and water. From the last it separates in fluffy white needles which melt, with decomposition, at about 126°. The analyses gave no concordant results, since it is not possible to recrystallize it without partial decomposition into the monosulphone and the sulphinic acid. It was found, however, that in ethereal solution 1 molecule of cinnamic aldehyde combines with exactly 2 molecules of paratoluenesulphinic acid.

IV. Addition of Sulphinic Acids to 1,2-Unsaturated Acids.

2. Addition of Paratoluenesulphinic Acid to Cinnamic Acid : β-Paratolylsulphonehydrocinnamic Acid, $C_6H_5CHCH_2CO_2H$.—

$$C_7H_7SO_2$$
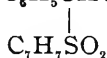
Equivalent quantities of paratoluenesulphinic acid and cinnamic acid were boiled in water, in a flask connected with an inverted condenser. Both acids melted to an oil under water. This oil gradually solidified, and after boiling for three days none was left. The solid was then filtered off and treated with a hot solution of sodium carbonate, in which nearly all of it dissolved. The part that was insoluble in the solution of sodium carbonate was repeatedly crystallized from alcohol and thus separated into paratolyldisulphoxide and distyrene. Since the former is always formed when the sulphinic acid is heated with water, and the latter when solutions of cinnamic acid are boiled, these substances are not connected with the principal reaction.

On cooling the hot solution in sodium carbonate a sodium salt separated as a heavy, white precipitate. This was dried on a porcelain plate, the dry salt extracted with boiling ether, and the residue dissolved in water. From this solution dilute sulphuric acid precipitated an acid which was recrystallized from large quantities of boiling water and analyzed.

0.1608 gram substance gave 0.3719 gram CO_2 and 0.0725 gram H_2O.

	Calculatrd for $C_{16}H_{18}SO_4$.	Found.
C	63.15	63.08
H	5.26	5.02

The acid was evidently formed by the direct union of 1 molecule of cinnamic acid and 1 molecule of the sulphinic acid. To locate the sulphone group the following method was used. Fittig found that hydrobromic acid combines with cinnamic acid to form β-bromhydrocinnamic acid. This acid, when treated with sodium toluenesulphinate, should give a β-sulphonehydrocinnamic acid which could be compared with the acid obtained by addition. We found, however, that the bromo-acid is decomposed by the sulphinate in the same way n which it is decomposed by carbonates :

$$C_6H_5CHBrCH_2CO_2H + RSO_2Na =$$
$$C_6H_5CH=CH_2 + C_7H_7SO_2H + NaBr + CO_2.$$
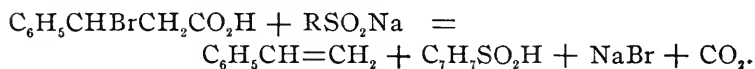
To guard against this decomposition we tried the methyl ester in place of the acid itself.

Cinnamic acid was dissolved in absolute methyl alcohol and the solution saturated with hydrobromic acid. The methyl ester of β-bromhydrocinnamic acid crystallized out on standing. Equivalent quantities of this methyl ester and the sodium salt of paratoluenesulphinic acid were dissolved in methyl alcohol and the solution boiled until there was no further separation of sodium bromide. The liquid was filtered, the filtrate evaporated to dryness, and the residue recrystallized from ether. The pure ester obtained in this way was saponified by boiling it with dilute hydrochloric acid until everything had gone into solution. The acid which crystallized on cooling this solution was the same as that which had been obtained by addition; the latter, therefore, has the sulphone group in the β-position with reference to carboxyl. A better way to prepare the substance is to heat the mixture of cinnamic and sulphinic acids with water in sealed tubes to 110°. The solid that separates contains a much smaller amount of by-product.

β-Paratolylsulphonehydrocinnamic acid is almost insoluble in cold water ; it dissolves slowly in boiling water, from which it separates, on cooling, in fine needles. It is readily soluble in alcohol and ether, very slightly soluble in ligroin. It is most easily purified through the sodium salt. It melts at 197° to 198° without decomposition.

The *sodium salt* was prepared by dissolving the acid in a hot solution of sodium carbonate, from which the salt separated on cooling. It was dried and crystallized from boiling alcohol. The analyses show that it contains 2 molecules of water of crystallization, only one of which can be driven off without decomposing the salt:

   I. 0.1301 gram salt gave 0.0254 gram Na_2SO_4.
  II. 0.0877 gram salt gave 0.0172 gram Na_2SO_4.
 III. 0.2174 gram salt gave 0.0117 gram H_2O at 130°.
  IV. 0.2057 gram dried salt gave 0.0437 gram Na_2SO_4.

	Calculated for $C_{16}H_{15}O_4SNa.2H_2O$.	I.	Found. II.	III.
Na	6.35	6.32	6.35	....
H_2O (1 mol.)	5.00	....	....	5.30

	Calculated for $C_{16}H_{15}O_4ONa.H_2O$.	Found.
Na	6.68	6.88

The salt crystallizes from alcohol in fine, white needles. It has an exceedingly bitter taste.

The *calcium salt*, made by boiling the acid with calcium carbonate suspended in water, crystallizes in plates. It is moderately soluble in water.

   I. 0.1683 gram salt gave 0.0330 gram $CaSO_4$.
  II. 0.1198 gram salt gave 0.0239 gram $CaSO_4$.

	Calculated for $(C_{16}H_{15}O_4S)_2Ca$.	I.	Found. II.
Ca	6.18	5.73	5.85

The *barium salt*, made like the calcium salt, crystallizes with 4 molecules of water of crystallization.

   I. 0.1258 gram substance gave 0.0356 gram $BaSO_4$.
  II. 0.0770 gram substance gave 0.0216 gram $BaSO_4$.
 III. 0.1220 gram substance lost 0.0110 gram at 15°.

	Calculated for $(C_{16}H_{15}SO_4)_2Ba$.	I.	Found. II.	III.
Ba	16.78	16.62	16.49	....
$4H_2O$	8.83	....	....	9.00

The *methyl ester* was made by boiling the acid with a 3 per cent solution of hydrochloric acid in methyl alcohol. It crystallizes from methyl alcohol in fine, white needles, which melt at 156°.

0.1989 gram substance gave 0.4660 gram CO_2 and 0.1010 gram H_2O.

	Calculated for $C_{17}H_{18}SO_4$.	Found.
C	64.15	63.89
H	5.63	5.64

The ester is not decomposed by boiling with water. Boiling hydrochloric acid saponifies it, and boiling caustic potash decomposes it into the potassium salt of paratoluenesulphinic acid and methyl cinnamate.

2. Addition of Benzenesulphinic Acid to Cinnamic Acid:
β-Phenylsulphonehydrocinnamic Acid, $C_6H_5CHCH_2CO_2H$.—A
$$SO_2C_6H_5$$
mixture of the two acids was suspended in water and the liquid boiled for several days. The product was purified by recrystallization from boiling water, from which it separated in shining plates melting at 173°.

0.2542 gram substance gave 0.5770 gram CO_2 and 0.1123 gram H_2O.

	Calculated for $C_{15}H_{14}SO_4$.	Found.
C	62.00	61.80
H	4.83	4.84

The acid is readily soluble in alcohol and ether ; very slightly in ligroin.

The *barium salt* crystallizes in needles, moderately soluble in water, insoluble in alcohol.

0.0993 gram salt gave 0.0310 gram $BaSO_4$.

	Calculated for $(C_{15}H_{13}SO_4)_2Ba$.	Found.
Ba	18.60	18.40

The *ethyl ester* was made by saturating with hydrochloric acid a solution of the acid in absolute alcohol. It crystallizes from alcohol in small, white needles melting at 139°.

I. 0.1486 gram substance gave 0.3490 gram CO_2 and 0.0764 gram H_2O.

II. 0.1314 gram substance gave 0.3078 gram CO_2 and 0.0670 gram H_2O.

	Calculated for $C_{17}H_{18}SO_4$.	Found. I.	II.
C	64.15	64.05	63.89
H	5.63	5.54	5.66

The ester is not changed by protracted boiling with water. When boiled with dilute hydrochloric acid it is saponified to the corresponding acid. When boiled with a dilute solution of caustic potash it is decomposed into cinnamic and benzene-sulphinic acids.
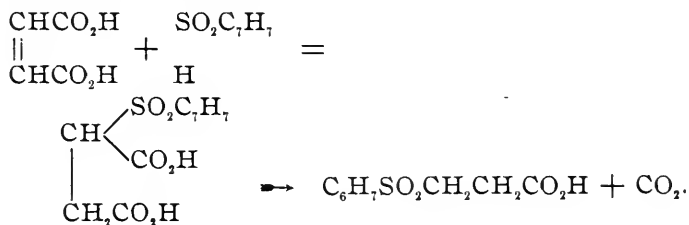
3. Addition of Paratoluenesulphinic Acid to Fumaric and Maleic Acids : β-Paratolylsulphonepropionic Acid,

$C_7H_7SO_2CH_2CH_2CO_2H$.—An aqueous solution containing paratoluenesulphinic acid and fumaric acid in molecular proportions was boiled until the oil that separated at first had completely solidified. The product was dissolved in a solution of sodium carbonate, the solution extracted with ether, and the acid reprecipitated with dilute sulphuric acid. After crystallization from hot water it gave the following results on analysis :

0.1819 gram substance gave 0.3536 gram CO_2 and 0.0990 gram H_2O.

	Calculated for $C_{10}H_{12}SO_4$.	Found.
C	52.58	53.01
H	5.31	6.03

These results indicated that the substance was not an addition-product, but a monobasic acid formed from the addition-product by loss of carbon dioxide :

$$\begin{array}{c} \mathrm{CHCO_2H} \\ \| \\ \mathrm{CHCO_2H} \end{array} + \begin{array}{c} \mathrm{SO_2C_7H_7} \\ \\ \mathrm{H} \end{array} =$$

$$\begin{array}{c} \mathrm{CH} {\Large\langle} \begin{array}{l} \mathrm{SO_2C_7H_7} \\ \mathrm{CO_2H} \end{array} \\ | \\ \mathrm{CH_2CO_2H} \end{array} \longrightarrow \; C_6H_7SO_2CH_2CH_2CO_2H + CO_2.$$

Since repeated recrystallizations failed to give an acid that had a sharp melting-point or that gave concordant results on analysis, maleic acid was substituted for fumaric acid in the

hope that the latter would give the same product without requiring the prolonged boiling necessary with the former. It was found that maleic acid, as expected, gave the same product as fumaric acid, but the substance was just as impure and just as difficult to purify as that obtained from fumaric acid. It melted from 107° to 115°.

The same acid was, however, obtained in a pure condition by treating β-iodopropionic acid with the sodium salt of paratoluenesulphinic acid. Fifty grams of β-iodopropionic acid were exactly neutralized with a solution of sodium carbonate, the calculated amount of the sulphinate was added to this solution, and the whole evaporated to dryness on the water-bath. The dark, reddish-brown residue was dissolved in dilute hydrochloric acid and the solution decolorized with boneblack. On evaporating the solution slowly the acid separated in needles melting at 110° to 113°.
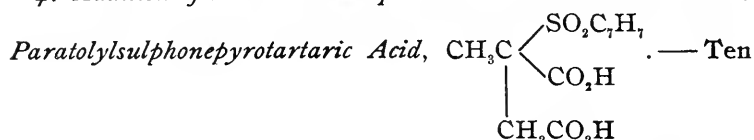
I. 0.2237 gram substance gave 0.4280 gram CO_2 and 0.1076 gram H_2O.

II. 0.1167 gram substance gave 0.2248 gram CO_2 and 0.0589 gram H_2O.

	Calculated for $C_{10}H_{12}SO_4$.	I.	II.
		Found.	
C	52.58	52.18	52.53
H	5.31	5.34	5.51

The acid was found identical with that obtained from fumaric acid and maleic acid. It is partially decomposed by repeated crystallizations from boiling water, the melting-point becoming considerably lower. This explains the difficulty in getting a pure product.

4. Addition of Paratoluenesulphinic Acid to Citraconic Acid :

Paratolylsulphonepyrotartaric Acid, $\mathrm{CH_3C}\left\langle\begin{array}{l}\mathrm{SO_2C_7H_7}\\\mathrm{CO_2H}\end{array}\right.$. — Ten

$\mathrm{CH_2CO_2H}$

grams of citraconic acid and 13.5 grams of paratoluenesulphinic acid were heated with water for two days at 110°. The liquid was then exactly neutralized with sodium carbonate, the solution extracted with ether, and evaporated to dryness.

The residue was dissolved in as small a quantity as possible of 50 per cent alcohol and this solution poured into an equal volume of absolute alcohol. The sodium salt precipitated at once. It was recrystallized by the same method. It separated in fine, white needles, containing 2 molecules of water of crystallization.

    I. 0.2377 gram substance gave 0.0936 gram Na_2SO_4.

    II. 0.2140 gram substance gave 0.0833 gram Na_2SO_4.

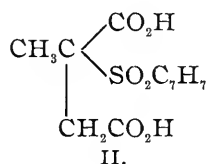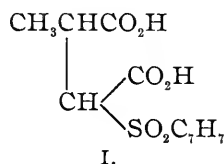   III. 0.3277 gram substance lost 0.0326 gram at 150°.

	Calculated for $C_{11}H_{12}SO_6Na_2.2H_2O$.	I.	Found. II.	III.
Na	12.60	12.65	12.65	....
$2H_2O$	9.84	....	....	9.97

On acidifying the aqueous solution of the sodium salt the acid separated as an oil. This was taken up with ether, and ligroin added slowly until the solution became slightly cloudy. On addition of a drop of ether the solution cleared up and the acid separated in small, lustrous prisms.
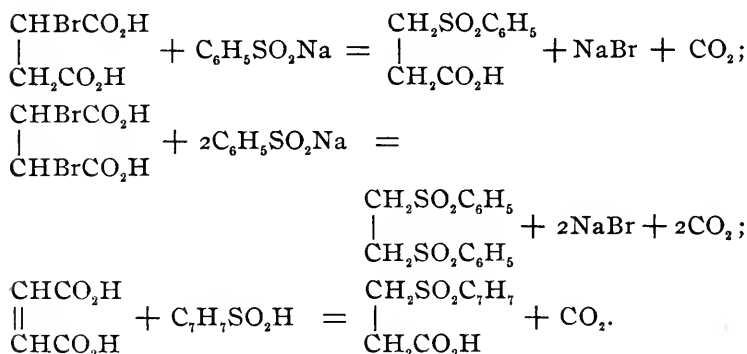
0.4118 gram substance gave 0.2226 gram CO_2 and 0.0979 gram H_2O.

	Calculated for $C_{12}H_{14}SO_6$.	Found.
C	50.35	50.45
H	4.89	4.88

The acid is extremely soluble in alcohol, ether, and acetone. It is insoluble in ligroin and chloroform. If precipitated from its solution in sodium carbonate it separates as an oil which does not solidify. It melts at 169° to 171°, and begins to lose carbon dioxide as soon as melted. An attempt to determine the structure of the acid by driving off carbon dioxide and identifying the residue failed because the acid broke down completely. The two possible formulas for the acid are :

CH_3CHCO_2H
|
$CH\begin{cases} CO_2H \\ SO_2C_7H_7 \end{cases}$
    I.

$CH_3C\begin{cases} CO_2H \\ SO_2C_7H_7 \end{cases}$
|
CH_2CO_2H
    II.

Formula I. represents a mode of linkage which is known to be exceedingly unstable. The following equations illustrate a number of cases in which such a substance would be expected but where a decomposition-product is invariably obtained :

$$
\begin{array}{l}
\text{CHBrCO}_2\text{H} \\
| \qquad\qquad\quad + \text{C}_6\text{H}_5\text{SO}_2\text{Na} = \\
\text{CH}_2\text{CO}_2\text{H}
\end{array}
\begin{array}{l}
\text{CH}_2\text{SO}_2\text{C}_6\text{H}_5 \\
| \qquad\qquad + \text{NaBr} + \text{CO}_2; \\
\text{CH}_2\text{CO}_2\text{H}
\end{array}
$$

$$
\begin{array}{l}
\text{CHBrCO}_2\text{H} \\
| \qquad\qquad\quad + 2\text{C}_6\text{H}_5\text{SO}_2\text{Na} = \\
\text{CHBrCO}_2\text{H}
\end{array}
$$

$$
\begin{array}{l}
\text{CH}_2\text{SO}_2\text{C}_6\text{H}_5 \\
| \qquad\qquad + 2\text{NaBr} + 2\text{CO}_2; \\
\text{CH}_2\text{SO}_2\text{C}_6\text{H}_5
\end{array}
$$

$$
\begin{array}{l}
\text{CHCO}_2\text{H} \\
\| \qquad\qquad\; + \text{C}_7\text{H}_7\text{SO}_2\text{H} = \\
\text{CHCO}_2\text{H}
\end{array}
\begin{array}{l}
\text{CH}_2\text{SO}_2\text{C}_7\text{H}_7 \\
| \qquad\qquad + \text{CO}_2. \\
\text{CH}_2\text{CO}_2\text{H}
\end{array}
$$

As the acid in question is stable in solution and does not lose carbon dioxide below its melting-point, there can be little doubt that its structure is represented by II.

V. Addition of Paratoluenesulphinic Acid to Unsaturated Ketones.

Paratoluenesulphinic acid combines with unsaturated ketones with most surprising ease. When the acid and an unsaturated ketone are brought together in any organic medium the liquid almost immediately becomes warm, and in a very short time the sparingly soluble sulphoneketone crystallizes out in characteristic long, fine needles, which fill the entire liquid.

1. Addition of Paratoluenesulphinic Acid to Benzalacetone, $\text{C}_6\text{H}_5\text{CHCH}_2\text{COCH}_3$

$\qquad$ | $\qquad\qquad\qquad$.—The sulphoneketone was made by
$\quad\; \text{SO}_2\text{C}_7\text{H}_7$
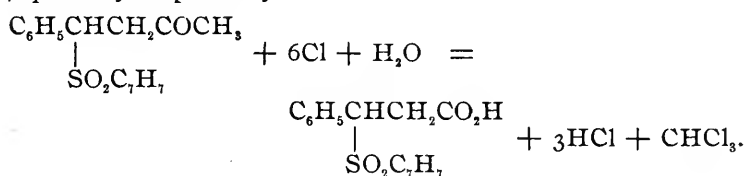
bringing the components together in alcoholic solution and recrystallizing the product from alcohol.

0.2322 gram substance gave 0.5737 gram CO_2 and 0.1251 gram H_2O.

	Calculated for $C_{17}H_{18}SO_3$.	Found.
C	67.54	67.38
H	5.96	5.98

The compound is readily soluble in acetone ; moderately soluble in boiling alcohol and boiling benzene ; insoluble in water. It separates from hot alcohol in fine, white needles, which pass into a more compact form when allowed to remain in contact with the cold solution.

The sulphoneketone slowly dissolves in a warm solution of bleaching powder, which breaks it down into chloroform and β-paratolylsulphonehydrocinnamic acid :

$$C_6H_5CHCH_2COCH_3$$
$$|$$
$$SO_2C_7H_7$$
$$+ 6Cl + H_2O =$$

$$C_6H_5CHCH_2CO_2H$$
$$|$$
$$SO_2C_7H_7$$
$$+ 3HCl + CHCl_3.$$

The chloroform is obtained by distillation ; the acid crystallizes out on acidifying the cold solution. This result shows that the sulphone group is in the β-position with reference to the carbonyl group.

The sulphoneketone can be boiled with dilute acids without appreciable change, but dilute alkalies rapidly decompose it. Thus, when a small quantity of the ketone was suspended in a solution of potassium hydroxide and the liquid distilled, a mixture of benzalacetone and its decomposition-products, benzaldehyde and acetone, passed off with the steam while the potassium salt of paratoluenesulphinic acid went into solution. A similar change takes place when the substance is treated with phenylhydrazine.

Two grams of the compound and 0.7 gram of phenylhydrazine were dissolved in alcohol and the solution boiled for several hours. On partly evaporating the solution two kinds of crystals separated : some very soluble in cold ether, and smaller crystals soluble only in boiling ether. The mixture was separated by repeated extraction with cold ether.

The ethereal solution was mixed with a little alcohol and the mixture evaporated until all the ether had been driven

off. Water was then added until the solution became cloudy. On cooling this solution, a substance separated in long needles of a bright lemon-yellow color. The melting-point (159°) indicated the phenylhydrazone of benzalacetone, and this was confirmed by comparing the substance with a preparation made directly from the ketone.

The crystals which were not dissolved by the cold ether were recrystallized from boiling ether and analyzed.

0.1126 gram substance gave 0.2450 gram CO_2 and 0.0563 gram H_2O.

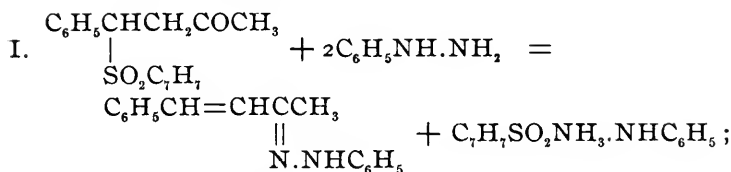|	Calculated for $C_7H_7SO_2H.C_6H_5NH.NH_2$.	Found.
C	59.08	59.32
H	6.06	5.55

That the substance is the phenylhydrazine salt of para-toluenesulphinic acid was established by comparing it with a specimen made directly from the acid. The salt crystallizes in needles. It melts with decomposition at 160° to 165°.

The mother-liquor, from which the hydrazone and the salt just described had separated, deposited a third substance on slow evaporation. After purification from alcohol this was obtained in long, branching, straw-colored crystals, which melted without change at 114°. An analysis gave the following results:

0.2031 gram substance gave 0.6047 gram CO_2 and 0.1251 gram H_2O.

	Calculated for $C_{16}H_{16}N_2$.	Found.
C	81.35	81.19
H	6.78	6.84

The compound gives a deep blue color with nitrous acid, and the characteristic reddish-purple color of the pyrazol derivatives when treated with ferric chloride in acid solution. It is 1,5-diphenyl-3-methylpyrazoline. The action of phenylhydrazine on the sulphoneketone is represented by the following equations:

I. $\quad \begin{array}{l} C_6H_5CHCH_2COCH_3 \\ \quad\quad | \\ \quad SO_2C_7H_7 \end{array} + 2C_6H_5NH.NH_2 =$

$\quad \begin{array}{l} C_6H_5CH=CHCCH_3 \\ \quad\quad\quad\quad || \\ \quad\quad\quad N.NHC_6H_5 \end{array} + C_7H_7SO_2NH_3.NHC_6H_5 \,;$

II. $\quad \begin{array}{l} C_6H_5CHCH_2COCH_3 \\ \quad\quad | \\ \quad SO_2C_7H_7 \end{array} + 2C_6H_5NH.NH_2 =$

$\quad C_6H_5N\underset{N=C(CH_3)}{\overset{CH(C_6H_5)}{<>}}CH_2 + C_7H_7SO_2NH_3NHC_6H_5.$
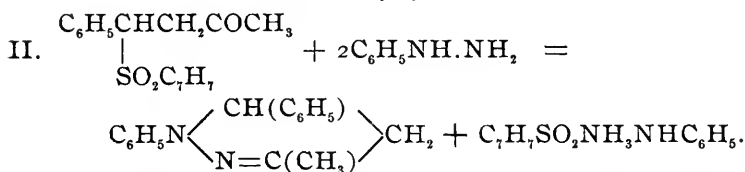
2. Addition of Paratoluenesulphinic Acid to Dibenzalacetone,
$\begin{array}{l} C_6H_5CHCH_2COCH=CHC_6H_5.\text{—A} \\ \quad | \\ \quad SO_2C_7H_7 \end{array}$ solution of the sulphinic

acid in alcohol was mixed with a solution of the ketone in the same solvent. The mixture was allowed to stand in the cold. The yellow color due to the unsaturated ketone gradually disappeared and a solid separated in the long, fine needles characteristic of these sulphoneketones. After recrystallization from alcohol the substance, which melted at 189°, gave the following results on analysis :

9.1856 gram substance gave 0.5020 gram CO_2 and 0.0973 gram H_2O.

	Calculated for $C_{17}H_{14}O.C_7H_7SO_2H.$	Found.
C	73.84	73.76
H	5.64	5.82

The substance is evidently a monosulphone. Its structure was established by oxidizing it with potassium permanganate. One and six-tenths grams of the permanganate were added to a solution of 2 grams of the substance in glacial acetic acid and the mixture heated on the water-bath for an hour. The dark-brown solution, which had a strong odor of benzaldehyde, was decolorized with sulphur dioxide. The pasty, white mass that separated was dissolved by addition of water. After removing benzaldehyde and benzoic acid by passing a current of steam through the solution, it was cooled, when an acid separated in needles. After purification through the

sodium salt this was found to be β-paratolylsulphonehydrocinnamic acid, showing that in the sulphoneketone the sulphone group is in the β-position. Many attempts were made to add a second molecule of sulphinic acid to the sulphoneketone or to add 2 molecules of the sulphinic acid to the unsaturated ketone, but all of them failed. This is remarkable, since the monosulphone readily combines with 2 atoms of bromine. Eight-tenths of a gram of bromine were added to 2 grams of the sulphone dissolved in chloroform and the liquid set aside until the color of bromine had disappeared. The chloroform was then evaporated and the residue recrystallized from alcohol. A bromine determination gave the following result :

0.1557 gram substance gave 0.1058 gram AgBr.

	Calculated for $C_{24}H_{22}SBr_2O_3$.	Found.
Br	29.09	28.85

The bromine addition-product crystallizes from alcohol in needles closely resembling the original substance. It is very soluble in chloroform ; moderately soluble in alcohol ; insoluble in ether, acetone, and glacial acetic acid.

3. Addition of Paratoluenesulphinic Acid to Benzalacetophenone.—One gram of the sulphinic acid was added to a solution of 1 gram of benzalacetophenone in alcohol. A white, crystalline solid separated at once. It was recrystallized from alcohol and analyzed.

0.2574 gram substance gave 0.6826 gram CO_2 and 0.1186 gram H_2O.

	Calculated for $C_{22}H_{20}SO_3$.	Found.
C	72.52	72.32
H	5.49	5.12

The substance crystallizes in needles melting at 169° to 170°.

4. Addition of Paratoluenesulphinic Acid to Cinnamylideneacetone, $C_6H_5CH : CH.CHCH_2COCH_3$.—Cinnamylideneacetone

$$\underset{SO_2C_7H_7}{\overset{|}{}}$$
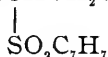
contains the combination of single and double linkages which Thiele[1] has called "a conjugated system of vicinal double unions." When it combines with 1 molecule of a sulphinic acid, the sulphone group ought, according to Thiele's theory, to go into the δ-position. The following results show that this is not the case; the sulphone group goes into the β-position.

Equivalent quantities of cinnamylideneacetone and para-toluenesulphinic acid were dissolved in cold acetone. The addition-product began to separate in a few minutes, and the reaction was complete in less than half an hour. The product, after crystallization from alcohol, melted at 125° to 126°. An analysis gave the following results :
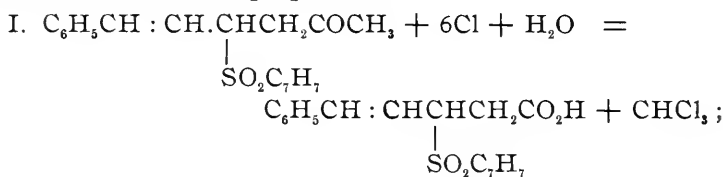
0.2036 gram substance gave 0.5175 gram CO_2 and 0.1122 gram H_2O.

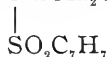|	Calculated for $C_{19}H_{20}SO_3$.	Found.
C	69.50	69.33
H	6.09	6.12

When the finely powdered sulphoneketone was warmed with a concentrated solution of bleaching-powder it gave a number of different substances, some of which dissolved while others remained suspended in the liquid. The insoluble substances were filtered off and discarded. The excess of bleaching-powder in the solution was reduced with acid potassium sulphite, the solution acidified with dilute hydrochloric acid, and repeatedly extracted with ether. The ether, on evaporation, left an oily residue containing benzoic acid, an unsaturated acid, and one or more acids containing halogen. The oil was suspended in water and distilled in a current of steam. Pure benzoic acid was carried into the distillate. The residue from the benzoic acid was dissolved in ether and the dry ethereal solution allowed to evaporate slowly. Only oils separated and all efforts to get solid substances from the oils failed. The entire residue was therefore dissolved in potassium hydroxide and carefully treated with potassium permanganate until the purple color of the permanganate no longer disappeared in the cold. The excess of permanganate

[1] Ann. Chem. (Liebig), **306**, 53.

and the oxides of manganese were then reduced with acid potassium sulphite and the solution made strongly acid with sulphuric acid. The oxidation-product crystallized out in long, brittle needles melting at 113°. Analyses, melting-point, and properties showed that the substance is β-para-tolylsulphonepropionic acid. This result proves that when the sulphinic acid combines with the ketone the sulphone group goes into the β-position. The successive steps are shown by the following equations:

I. $C_6H_5CH : CH.CHCH_2COCH_3 + 6Cl + H_2O =$
$$\overset{|}{SO_2C_7H_7}$$
$$C_6H_5CH : CHCHCH_2CO_2H + CHCl_3 ;$$
$$\overset{|}{SO_2C_7H_7}$$

II. $C_6H_5CH : CH.CHCH_2CO_2H + 4O =$
$$\overset{|}{SO_2C_7H_7}$$
$$C_6H_5CO_2H + HO_2CCHCH_2CO_2H ;$$
$$\overset{|}{SO_2C_7H_7}$$

III. $HO_2CCHCH_2CO_2H = C_7H_7SO_2CH_2CH_2CO_2H + CO_2.$
$$\overset{|}{SO_2C_7H_7}$$
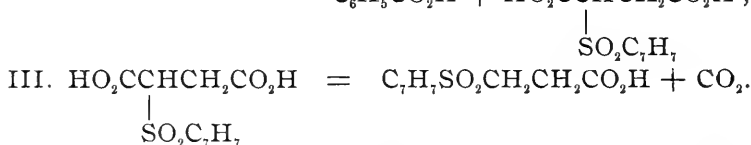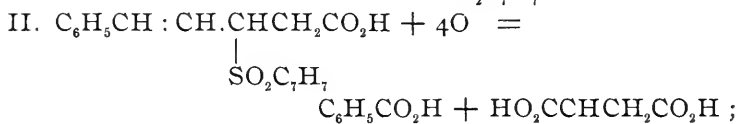
6. *Addition of Paratoluenesulphinic Acid to Cinnamylidene-acetophenone*, $C_6H_5CH : CH.CHCH_2COC_6H_5.$—The substances
$$\overset{|}{SO_2C_7H_7}$$
combine in the cold. The product crystallizes from acetone in needles that melt at 145°. An analysis gave the following results:

0.1860 gram substance gave 0.5023 gram CO_2 and 0.0972 gram H_2O.

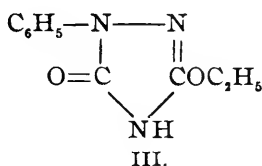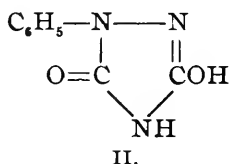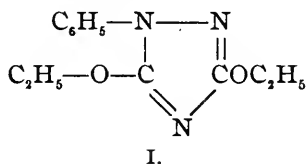|	Calculated for $C_{24}H_{22}O_3O.$	Found.
C	73.84	73.61
H	5.64	5.80

We expect to continue this work with acids that contain conjugated systems of double unions.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
November, 1903.

A NOTE ON SOME OF THE REACTIONS IN THE URAZOLE SERIES.

BY S. F. ACREE.

In a recent number of this JOURNAL[1] appeared an article by Wheeler and Johnson in which were described some experiments in the urazole series, the results of which depart widely from those obtained by the present writer. Wheeler and Johnson state that by the action of ethyl iodide on monosilver phenylurazole they were able to obtain 1-phenyl-3,5-diethoxyurazole[2] (I.) and phenylurazole (II.), but no 1-phenyl-3-ethoxyurazole (III.), which is indeed the chief product of the reaction. This 1-phenyl-3-ethoxyurazole (III.) was formerly[3] in hand in slightly impure state, and directions have been recently published[4] for obtaining it in a pure state by this very reaction.

$$C_6H_5-N----N$$
$$C_2H_5-O-C \qquad COC_2H_5$$
$$N$$
I.

$$C_6H_5-N----N$$
$$O=C \qquad COH$$
$$NH$$
II.

$$C_6H_5-N----N$$
$$O=C \qquad COC_2H_5$$
$$NH$$
III.

The cause of Wheeler and Johnson's failure to obtain the 1-phenyl-3-ethoxyurazole (III.) found by this reaction is at once clear from their article. This ethoxy derivative is the normal reaction-product, and they should have done their experimental work with the main object of securing this substance. From their article, one could suspect that they entirely overlooked the fact that such a substance could be formed. Although they say (p. 32) " It seemed incredible

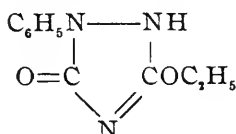[1] Wheeler and Johnson : This JOURNAL, 30, 24 (1903).
[2] Wheeler and Johnson : Loc. cit. ; Acree : Ber. d. chem. Ges., 36, 3148.
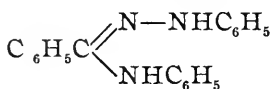[3] Acree : This JOURNAL, 27, 131 ; Ber. d. chem. Ges., 35, 559.
[4] Acree : Ber. d. chem. Ges., 36, 3146.

that a monoethyl derivative of phenylurazole should be insoluble in alkali,'' yet they dissolve this ethoxy derivative in alkali and discard this alkaline solution. They extracted an ethereal solution containing 1-phenyl-3,5-diethoxyurazole (insoluble in alkalies) and 1-phenyl-3-ethoxyurazole (soluble in alkalies) with an alkaline solution (p. 39), thereby removing the 1-phenyl-3-ethoxyurazole from the ethereal solution. They then examined the ethereal solution and found the 1-phenyl-3,5-diethoxyurazole (which melts at 53° instead of at 46° to 47°, as stated by Wheeler and Johnson). They evidently entirely forgot to examine the alkaline extraction-solution and thus failed to find the 1-phenyl-3-ethoxyurazole. If Wheeler and Johnson will repeat their work, using the suggestions above offered, the writer is sure that they will have no difficulty in obtaining the 1-phenyl-3-ethoxyurazole formed in this reaction.
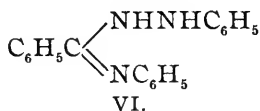
Wheeler and Johnson take exceptions to Acree's supposition that the substance 1-phenyl-2-hydro-3-ethoxyurazole (IV.) might exist as a definite compound, tautomeric with 1-phenyl-3-ethoxy-4-hydrourazole (III.). These writers believe that these two formulas probably represent the same substance. The possibility of this kind of tautomerism is proved beyond question by the isolation of just such tautomeric benzenyldiphenylhydrazidines[1] (V. and VI.) and the tautomeric methenylphenyltoluylamidines[2] (VII. and VIII.).
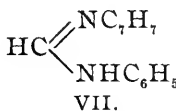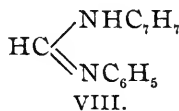
$$
\begin{array}{cc}
\underset{\text{IV.}}{\begin{array}{c} C_6H_5N\!\!-\!\!-\!\!NH \\ \;|\qquad\quad| \\ O\!=\!C\quad\;COC_2H_5 \\ \quad\diagdown\;\diagup \\ \qquad N \end{array}} &
\underset{\text{V.}}{C_6H_5C\!\!\diagup\!\!\diagdown\!\!\begin{array}{l} N\!-\!NHC_6H_5 \\ NHC_6H_5 \end{array}}
\end{array}
$$

$$
\underset{\text{VI.}}{C_6H_5C\!\!\diagup\!\!\diagdown\!\!\begin{array}{l} NHNHC_6H_5 \\ NC_6H_5 \end{array}}
\qquad
\underset{\text{VII.}}{HC\!\!\diagup\!\!\diagdown\!\!\begin{array}{l} NC_7H_7 \\ NHC_6H_5 \end{array}}
\qquad
\underset{\text{VIII.}}{HC\!\!\diagup\!\!\diagdown\!\!\begin{array}{l} NHC_7H_7 \\ NC_6H_5 \end{array}}
$$

That the form IV. can possibly rearrange into the form III., or *vice versa*, can hardly be doubted. Indeed it might very

[1] v. Pechmann : Ber. d. chem. Ges., **28**, 869, 2362.

[2] Walther : J. prakt. Chem., **55**, 41.

well be that the form IV. rearranges into the form III. under all conditions which we can easily realize, and that we cannot obtain it as a distinct substance, or can obtain it only with great difficulty. Although the substance has not yet been made, and predictions are unsafe, the present writer believes that this substance, as such, will not exhibit the acid properties possessed by the other known monoalkylphenylurazoles. If it forms stable neutral (in water) alkali salts, it will be because it undergoes rearrangement and forms salts somewhat like IX or X.

$$C_6H_5-N\underline{\quad\quad}N$$
$$Me-O-C\qquad COC_2H_5$$
$$N$$
IX.

$$C_6H_5N\underline{\quad\quad}N$$
$$Me-O-C\qquad COC_2H_5$$
$$N$$
X.
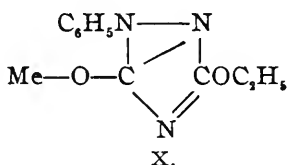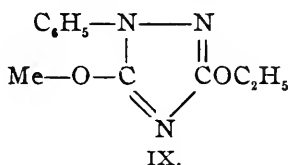
This does not mean that the writer believes it to be impossible to obtain the isomeric salts,

$$-NMe-C=O \quad\text{and}\quad -N=C-O-Me,$$
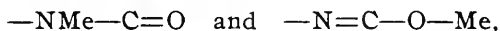
of these urazoles and other amides. Indeed, this very hypothesis was put forward over two years ago in the following words[1] to account for the properties of disodium phenylurazole: "Although the disodium salt can be formed by boiling phenylurazole with sodium alcoholate, in absolute alcohol, yet it gives a strongly alkaline reaction, when dissolved in water, indicating that one of the sodium atoms of the salt is joined to a nitrogen atom of the urazole ring."

Since then, Lander[2] has used a similar hypothesis to explain the reactions between alkyl haloids and the salts of tautomeric compounds. Hantzsch[3] has isolated two different mercury salts of cyanuric acid, and Titherly[4] has noticed similar phenomena in the silver salts of benzamide and acetamide.

Wheeler and Johnson state that by the action of a molecu-

[1] Acree : This JOURNAL, **27**, 119.

[2] Lander : J. Chem. Soc. (London), **83**, 414 (1903).

[3] Hantzsch : Ber. d. chem. Ges., **35**, 2717 (1902).

[4] Titherly : J. Chem. Soc. (London), **79**, 409 (1901).

lar proportion of acetyl chloride on monosilver phenylurazole[1] they obtained a new diacetyl derivative of phenylurazole, but no monoacetyl derivative. A monoacetyl derivative should be, of course, the normal reaction-product. As published before,[2] the chief product of this reaction is monoacetylphenylurazole, which melts at 173°. This experiment has been repeated several times under widely varying conditions. Various samples of the monoacetyl derivative so obtained have been analyzed, and have been converted into 1-phenyl-4-methylacetylurazole by means of diazomethane. The writer has used very pure silver phenylurazole in these experiments. As Wheeler and Johnson state that their silver phenylurazole contained 39 per cent silver instead of 37.9 per cent, the writer believes that their results differ from ours on account of the impurities (possibly some disilver phenylurazole) in their silver salt.

Small quantities of diacetylphenylurazole and of phenylurazole are generally obtained as by-products. This is entirely analogous to the formation of 1-phenyl-3,5-diethoxyurazole and phenylurazole as by-products in the reaction between silver phenylurazole and ethyl iodide, 1-phenyl-3-ethoxyurazole being the chief product of the reaction. The formation of these small quantities of by-products has been explained in a previous paper.[3]

The writer can only suggest that if Wheeler and Johnson will repeat their work, using pure silver phenylurazole, they will obtain the same results that the present writer has above described.

UNIV. OF BERLIN, Nov. 1, 1903.

REVIEWS.

AUSGEWÄHLTE METHODEN DER ANALYTISCHEN CHEMIE. Von PROF. DR. A. CLASSEN. Zweiter Band. Braunschweig : Friedrich Vieweg und Sohn. 1903. pp. xvi + 831.

The first volume of this work was reviewed in this JOURNAL for May, 1901 (Vol. XXV., p. 437). It was devoted mainly

[1] Wheeler and Johnson : This JOURNAL, **30**, 37.

[2] Acree : Ber. d. chem. Ges., **36**, 3143 (foot-note).

[3] Acree : *Ibid.*, **36**, 3147.

to processes for the detection and determination of the metallic elements and their compounds. The second volume covers like ground for the non-metals. The field is for the most part restricted to compounds usually spoken of as inorganic, though methane, ethylene, and acetylene are included, as also the cyanides and compound cyanides, and the methods of ultimate or elementary organic analysis. Notice is taken of sundry substances of which our knowledge has been acquired within recent years, as for example, the long unobserved atmospheric gases—helium, neon, argon, krypton, and xenon (the characteristic spectra of which are shown in a well-printed table in colors),—the percarbonates, persulphates, and carborundum.

The larger part of the matter is drawn from German sources, although methods originating elsewhere than in Germany are not altogether neglected. Thus attention is given to some of the processes suggested by Hillebrand and Gooch in this country.

In regard to the degree of fulness with which methods of technical interest are treated there seems to be some inequality. The examination of ordinary potable water and of mineral waters takes up 117 pages, while but 15 pages are given to the important subject of explosives. No attempt appears to have been made to supplement matters treated of in the first volume by adding the results of more recent researches. For example, there is no account of the lately developed improvements in methods for the detection of minute quantities of arsenic in beer and other complex organic mixtures.

On the whole, however, the new volume contains much useful and valuable information, and, like its precursor, is handsomely printed and illustrated. J. W. M.

GRUNDRISS DER REINEN UND ANGEWANDTEN ELEKTROCHEMIE. Von P. FERCHLAND, Dr. Phil. Mit 59 Figuren im Text. Halle a. S. Verlag von Wilhelm Knapp. pp. 271. 1903.

The book in hand is an elementary treatise on electrochemistry. The scope of the work is not widely different from that of several books in this field. The more important chapters deal with : The Law of Faraday, Transference Numbers, Conductivity, Theories of Electrolysis, The Theory of Electrolytic Dissociation, Calculation and Measurement of Electromotive Force, The New Theory of Electrolysis, Absolute Differences in Potential and Polarization.

The book is clearly and judiciously written, and will doubtless find its place in the literature of electrochemistry.

H. C. J.

A Text-Book of Organic Chemistry. By Dr. A. F. Holleman, Professor Ordinarius in the University of Groningen, Netherlands. Translated from the second Dutch Edition by A. Jamieson Walker, Ph.D. (Heidelberg), B. A., Head of the Department of Chemistry, Municipal Technical College, Derby, England, assisted by Owen E. Mott, Ph.D. (Heidelberg), Demonstrator of Chemistry, Municipal Technical College, Derby, England. With the co-operation of the Author. First Edition, First Thousand. New York : John Wiley & Sons ; London : Chapman & Hall, Limited. 1903. pp. xvii + 555. Price, $2.50.

The author gives in his preface some of his reasons for writing this book : '' Most of the short text-books of organic chemistry contain a great number of isolated facts. The number of compounds described in them is so considerable as to confuse the beginner. Moreover, the theoretical grounds on which the division of the science is based are often kept in the background ; for example, the proofs given of the constitutional formula frequently leave much to be desired. However useful their books may be for reference, they are often ill-suited for text-books, as many students have learned from their own experience.

'' In this book I have endeavored to keep the number of unconnected facts within as narrow limits as possible and to give prominence to the theory underlying the subject. For this reason a proof of the structure of most of the compounds is given.'' * * * '' The book is essentially a text-book, and makes no claim to be a '' Beilstein'' in a very compressed form.''

The book undoubtedly has much to recommend it. It is clearly written and the subject is treated in a thoroughly scientific way and yet not pedantically. It is not so thoroughly scientific as to be uninteresting.

The general arrangement is much like that commonly adopted. The division into '' The Fatty Compounds'' and '' The Aromatic Compounds and Substances Related to Them'' is retained, and the classification of compounds under these heads makes no claim to originality.

While the translation, on the whole, is smooth, there are some passages that will give trouble. On page 391 occurs this statement : '' It has been proved that no isomers of ketoximes, $\overset{R}{\underset{R'}{\diagup}}C : NOH$, exist, when R and R' are similar, two isomers are known when these groups are dissimilar.'' This is not clear nor is it true. It is true, however, that when R$=$R', when R and R' are the same (not similar), no isomers exist.

Again, on page 101, the following is given as the proof that "the acids $C_nH_{2n}O_2$ contain the group $-C\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagup}}$ linked to an alkyl-radicle": "It was stated in **82** that a solution of sodium-alkyl in zinc-alkyl is obtained when sodium reacts with the latter. When a stream of dry carbon dioxide is passed into this solution there is formed the sodium salt of an acid which contains 1 carbon atom in the molecule more than the alkyl group. Thus, sodium methyl, CH_3Na, yields sodium acetate, $C_2H_3O_2Na$. This reaction may be explained by assuming that the sodium atom is released from the alkyl group and reacts with CO_2 becoming linked to one of its oxygen atoms, for which it possesses great affinity. In this way $C\overset{\displaystyle O}{\underset{\displaystyle O}{\diagup}}$ is converted into $-C\overset{\displaystyle O}{\underset{\displaystyle ONa}{\diagup}}$. Since this group, and also the alkyl-radicle from which the sodium atom has been separated have only one free carbon bond apiece it may be assumed that the two groups unite, forming a compound

$$C_nH_{2n+1}-C\overset{\displaystyle O}{\underset{\displaystyle ONa}{\diagup}} \text{ .''}$$
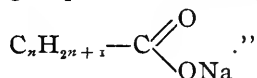
The reviewer is of the opinion that the beginner will worry over this a good deal. The lack of clearness in this case cannot be laid at the door of the translator alone. The author is partly responsible. The translator is not always consistent in the writing of names of compounds. A glaring case of inconsistency is to be found on page 116. The names of three esters are there given within the limits of three lines and they are printed thus : "isoamyl-valerate," "ethyl butyrate," and "isoamylacetate." This is confusing to the student and does not help him to overcome the slovenly habits with which he is usually endowed by nature.

The name "Brühl" is incorrectly given "Bruhl" on page 301.

In regard to the formula of benzene, the author gives the preference to the centric formula first proposed by Armstrong and afterwards adopted, for a time, by Baeyer. As Baeyer's work on the constitution of benzene advanced, however, he gave up the centric formula of Armstrong and expressed himself as in favor of the diagonal formula of Claus. The latest utterance of Baeyer on this subject justifies the belief that he still prefers the Claus formula to all others.

On page 78 the author says the word mercaptan is derived

from *corpus mercurio aptum*. This is a mistake. Mercaptan is derived from *corpus mercurium captans*. Zeise gave the name mercaptum to the radical C_2H_5S, of which, with hydrogen, he held mercaptan to be made up $H + C_2H_5S$. The word mercaptum was derived from *corpus mercurio aptum* [see Zeise, Ann. chim. phys., (2), **56**, 87 (1834)].

In brief, the book, like others, is not free from errors. Those that have been detected are not, however, serious, and they do not materially detract from the value of the book.

I. R.

PAPERS ON ETHERIFICATION AND ON THE CONSTITUTION OF SALTS. By ALEXANDER WILLIAMSON, LL.D., F.R.S. (1850–1856). Edinburgh: The Alembic Club; Chicago: The University of Chicago Press. 1902. Price, 40 cents.

The Alembic Club reprints are well known to chemists. This is the sixteenth issue. All the volumes thus far published are of fundamental importance, including, as they do, papers by Black, Dalton, Wollaston, Cavendish, Avogadro, Davy, Scheele, and other fathers of the science. Students of chemistry, young and old, are advised to buy every one of these volumes and read them over and over again. By an arrangement with the Alembic Club, they can now be obtained from the University of Chicago Press for a small price.

I. R.

A TEXT-BOOK OF VOLUMETRIC ANALYSIS. With special reference to the volumetric processes of the pharmacopoeia of the United States. Designed for the use of Pharmacists and Pharmaceutical Students. By HENRY W. SCHIMPF, Professor of Inorganic Chemistry in the Brooklyn College of Pharmacy. Fourth Edition, Revised and Enlarged. New York: John Wiley & Sons. 1903. pp. xxix + 553.

The third edition of this book was reviewed in this JOURNAL (**21**, 98). The present issue differs principally from the previous one by containing additional methods for the volumetric analysis of alkaloids. What was said in the previous review of the general character of the book applies at the present time with added force. One is more than ever impressed with the mechanical nature of the instructions and of the non-convincing character of the directions. Throughout the book the personal element, which plays so important a part in the successful text-book, appears to be lacking and it appears as a mere undigested compilation, for the most part badly expressed. That there has been a demand for a book of this kind, however, is evidenced by the fact that it has reached its fourth edition. H. F.

DIE ALUMINIUM INDUSTRIE. Von DR. F. WINTELER. Braunschweig: Friedrich Vieweg und Sohn. 1903. pp. xi + 108. Price, 6 marks.

This is one of those useful pamphlets which the Germans

know so well how to prepare. To those wishing to get a survey of the aluminium industry without searching through a mass of details in special treatises, or looking through the journals for the original articles, this book will be very valuable. It treats of the early history of the metal, its chemical and physical properties, the preparation of pure alumina from bauxite and kaolin, carbon electrodes, electric furnaces, the measurement of electric currents, the working of the metal and its uses.

While none of the chapters will serve as a complete guide, and specialists will complain because their particular field has been slighted, nevertheless much information has been condensed into the volume. It is indeed a very useful review of the patent and scientific literature of the aluminium industry. Incidentally, the author gives methods of analysis of bauxite, clay, cryolite, and commercial aluminium.   H. F.

ELEMENTS OF INORGANIC CHEMISTRY. By HARRY C. JONES, Associate Professor of Chemistry in the Johns Hopkins University. New York: The Macmillan Co. 1900. pp. 326.

The sympathies of every thoughtful, conscientious teacher must needs go out to the author who ventures to give us a new "Elements of Inorganic Chemistry." All will admit there is an abundance of material for such a book and an opportunity is not wanting, but the question is, *what* and *how much* to present ?

The fact that these questions have never been answered satisfactorily, together with the fact that every writer sees in ordinary chemical phenomena the chance to apply the pet theories of that particular branch of the science in which he himself is most interested, doubtless accounts for the ever increasing number of such publications.

In the book before us the attempt has been made to present the simpler aspects of chemical change from the standpoint of our more recent acquisitions in the domain of physical chemistry. To the author this point of view is the natural and normal one, and from his standpoint this is the normal and natural method of presenting the subject of chemistry to the mind of the young student. Whether it is the best method of presenting the subject of elementary chemistry, time and the experience of good teachers can alone decide. In the main, the original conception of the book has been well carried out and carefully executed. For a work of its kind, it contains much that is new and refreshing, and of necessity a good deal that is old. The plan of putting directions for experiments at the conclusion of each of the several topics treated of, so as to

not interfere with continuity in the presentation of the subject, must commend itself to student and instructor alike. A full and complete index also is not the least valuable of its many excellent features, and in mechanical execution it leaves but little to be desired.

In our opinion, however, not only is nothing gained, but something is distinctly lost, by presenting the physical properties of a substance at the close of each substance considered, as has usually been done.

Ordinarily, there is nothing included under this head that is not readily intelligible to the student as a quality or characteristic of the substance under consideration, and the arrangement adopted only serves needlessly to accentuate physical and chemical differences which in reality are intimately correlated. In our opinion this mode of presentation is not in harmony with the true spirit of physical chemistry.

J. H. K.

A LABORATORY GUIDE TO QUALITATIVE ANALYSIS WITH THE BLOW-PIPE. By F. W. MARTIN, PH.D. New York : John Wiley & Sons. 1903. pp. iv + 47.

After reading the author's preface one is left in doubt as to the class of readers for whom the book is intended since he says " this little volume is designed to be used, primarily, as a laboratory guide by students of qualitative analysis ; secondarily, as a work of reference by practising chemists ;" and later he writes, "this book is intended for the use of teachers who have a comprehensive knowledge of chemical facts and phenomena."

If the book be placed in the hands of the student of qualitative analysis without the supervision of a teacher with " comprehensive knowledge of chemical facts" its value is open to question, but if supplemented with explanations from the instructor it will prove a valuable adjunct to the usual course in wet methods. The author's attempt to bring dry methods to the attention of the teacher of qualitative analysis is certainly worthy of praise.

The use of such hybrids as " basigen" and " acidigen" is most unfortunate ; on p. 24 we read that " the bead has its surface *eaten* away by dilute acid" and that the " products of these *by-reactions* separate as minute crystals." It is questionable whether this book will find its way into the libraries of many practising chemists since all that it contains is to be found in larger and more complete works on blowpipe analysis.

As a companion to a text-book on qualitative analysis, however, this little work will surely find its place. F. H. G.

AMERICAN

CHEMICAL JOURNAL

OXIDATION AND REDUCTION IN THE ANIMAL ORGANISM AND THE TOXIC ACTION OF POWERFUL OXIDIZING AND RE- DUCING SUBSTANCES.

BY J. H. KASTLE AND ELIAS ELVOVE.[1]

It occurred to one of us (Kastle) that those changes ordi- narily included under the head of nitrification and denitrifica- tion could be brought about not only by certain micro-organ- isms but also by other life-forms, such as the higher plants and animals.

It was with this idea in mind that an experimental study of these changes was undertaken several months ago, and while the investigation has by no means been completed, some in- teresting results have already been reached, and in the pres- ent communication such of these will be considered as seem to throw light on the oxidation and reduction processes in the animal organism.

The Fate of Hyponitrites, Nitrites, and Nitrates in the Organ- ism.

As part of the problem originally before us, it occurred to us to investigate the conduct and fate of hyponitrites, nitrites,

[1] Research Assistant in the Carnegie Institution of Washington.

and nitrates in the body of higher animals. The rabbit was chosen for the experiments, but in one experiment a cat was employed. It has been found that when rabbits are fed on a diet of boiled oats their urine shows no reaction for nitrite or nitrate. On a diet of succulent vegetables, however, nitrates can be readily detected in the urine by the diphenylamine reaction. Hence, during the period of experimentation and for some time previous thereto, the animals in use were kept on a diet of boiled oats. During the progress of the experiment the animal was confined in a wire cage so arranged that the urine could be collected in a flat porcelain dish. The urine was examined as soon as passed so as to avoid any secondary bacterial changes that might take place on standing. Diphenylamine was employed in testing for nitrates and Griess' sulphanilic acid reagent was used in testing for nitrites. In some instances nitrates were tested for by removing any nitrite present by boiling the solution to be tested with ammonium chloride, then reducing with zinc dust, filtering, and testing the filtrate for nitrite with Griess' reagent.

Rabbits of uniform weight and size were selected for the experiments, weighing on the average 1 kilogram.

Experiment 1, with Sodium Hyponitrite.—Five-tenths gram sodium hyponitrite in 3 cc. of water was injected into a rabbit subcutaneously. The animal showed some signs of pain for some time after the injection, due in all probability to the alkali resulting from the decomposition of the hyponitrite. The skin around the wound made by the needle remained moist for some time after the injection and the liquid which exuded therefrom was found to have an alkaline reaction. The urine which was passed at intervals after the administration of the hyponitrite was tested immediately, but no nitrite or nitrate could be detected. The animal soon regained its normal condition.

Experiment 2, with Hyponitrous Acid.—After an interval of several days the rabbit employed in Experiment 1 was given a subcutaneous injection of 3 cc. of N/10 hyponitrous acid. The acid employed was prepared immediately before the experiment by treating N/10 hydrochloric acid with an excess

of pure silver hyponitrite and filtering off the silver chloride. The animal urinated in five hours after the injection. The urine was tested for nitrites and nitrates. It was found to contain large amounts of nitrate but no nitrite. The urine of this rabbit was then tested as fast as the specimens could be obtained for five days following the injection. No evidence of nitrite was obtained at any time during this interval. The nitrate showed a steady and regular diminution in amount from day to day until at the end of the third day following the injection the urine failed to show the nitrate test. While apparently in perfect health, the animal died suddenly on the fifth day following the administration of the hyponitrite, whether from the effects of this substance or from other causes could not be determined.

Experiment 3, with Hyponitrous Acid.—A second rabbit was injected subcutaneously with 3 cc. of N/10 hyponitrous acid. The animal passed urine in fifteen minutes after the injection. This also gave a good test for nitrate with diphenylamine, and also by the other test which consisted in reducing with zinc dust and testing for nitrite with Griess' reagent. The urine did not give the slightest test for nitrites. This rabbit also died several days after the injection.

Experiment 4, with Nitrous Acid.—Tenth-normal nitrous acid was prepared by adding an excess of pure silver nitrite to a known amount of N/10 hydrochloric acid and filtering off the silver chloride. This operation was conducted at 0° C. in order to prevent the decomposition of the nitrous acid. Three cc. of the acid were injected subcutaneously into a young rabbit. Three hours after the injection the animal urinated. The urine was found to contain large amounts of nitrates and traces of nitrites. Neither of these substances could be detected in the urine of the animal prior to the injection of the nitrous acid.

Experiment 5, with Sodium Nitrite.—A young rabbit was injected subcutaneously with 3 cc. of a normal solution of pure sodium nitrite. The animal showed signs of pain and discomfort immediately and passed urine in ten minutes after

the injection. This urine gave no test for nitrite or nitrate. About thirty minutes after the injection the animal died suddenly, passing urine just a few moments before its death. In this specimen both nitrates and nitrites were found in abundance. The relative amounts of nitrate and nitrite were determined colorimetrically with the result that about three times as much nitrate as nitrite was found to be present.

Experiment 6, with N/2 Sodium Nitrite.—A young rabbit, weighing 1050 grams, received 3 cc. of a N/2 solution of sodium nitrite subcutaneously. The animal urinated five hours after the injection. This was found to contain both nitrates and nitrites in the ratio of five of the former to one of the latter. The animal continued in good health as long as he was under observation and at no time after the injection were any disturbances noted.

Experiment 7, with N/10 Sodium Nitrite.—A young rabbit was injected subcutaneously with 3 cc. of a N/10 solution of sodium nitrite. The animal urinated five hours after the injection. On examination it was found to contain considerable amounts of nitrate and only traces of nitrite. A specimen of the urine obtained from the animal before the injection showed neither nitrate nor nitrite.

Experiment 8, with N/100 Sodium Nitrite.—Three cc. of N/100 sodium nitrite was injected into a young rabbit. As in Experiment 7, the urine obtained from the animal after the injection gave tests both for nitrate and nitrite, the former in much the larger amount.

Experiment 9, with N/1000 Sodium Nitrite.—A young rabbit was injected subcutaneously with 3 cc. N/1000 sodium nitrite. The animal passed urine eight hours after the injection. It was found to contain nitrate but no nitrite.

Experiment 10, with 2N Sodium Nitrite on a Cat.—Three cc. of 2N sodium nitrite was injected subcutaneously into a full-grown cat. At first the nitrite seemed to exert a hypnotic effect and for some moments after the injection the animal remained in a somewhat dazed and sleepy condition. Then followed an abundant secretion of tears, and for twenty minutes the animal remained quiet, at the end of which time it was

observed to suddenly collapse. Violent convulsions then set in and these continued uninterruptedly until death occurred in fifteen minutes after the first collapse. During the period of convulsions there was an involuntary movement of the bowels and an abundant flow of saliva. Some of the saliva was collected and found to contain both nitrates and nitrites, the former in relative larger amount. A few moments after the injection the animal passed urine. It gave no test for nitrate nor nitrite. The post-mortem examination showed the abdominal and thoracic organs to be normal. The left ventricle of the heart was found to be stiff and full of blood. The blood itself was dark chocolate-brown in color. The bladder was found to be empty. Several of the organs, including the bladder, kidneys, and liver, were cut up into small pieces and allowed to stand for a few moments in contact with water containing small amounts of toluene as antiseptic. Both nitrate and nitrite were found in the solutions thus obtained, the former in excess.

Experiment 11, with Nitric Acid.—Three cc. of N/10 nitric acid were injected subcutaneously into a young rabbit. The animal urinated in one hour after the injection. The urine was found to be slightly alkaline in reaction and to contain nitrates, together with smaller amounts of nitrites. No toxic symptoms were observable.

Experiment 12, with Potassium Nitrate.—Three cc. of normal potassium nitrate were injected into a young rabbit. Before the injection, the urine of the animal contained neither nitrate nor nitrite. Two hours after the injection the animal passed urine which had a slightly acid reaction and was found to contain nitrates but no nitrites.

Experiment 13, with a Saturated Solution of Sodium Nitrate. —Six and five-tenths cc. of a saturated solution of sodium nitrate, containing five grams of the salt, were injected subcutaneously into a young rabbit, weighing 950 grams. The concentrated salt solution caused considerable pain and local irritation at first. This soon passed off, however, and the animal passed into a semi-comatose condition, which increased until several hours before death the animal had passed into a

deep coma. Death occurred eighteen hours after the injection. In this quantity the nitrate caused great thirst and acted as a diuretic, the animal passing urine five times in the first ten hours after the injection. The urine which was passed one hour after the injection was found to contain only nitrates, while that passed two hours after the injection contained also traces of nitrite. The amount of nitrite in the urine continually and regularly increased from this time on, until that passed ten hours after the injection gave excellent tests for nitrite. The urine was slightly alkaline in reaction at all times and contained large amounts of nitrate. The post-mortem showed the various organs to be normal, and the blood retained its bright-red color. The bladder was full of clear urine having a slightly acid reaction. It gave an excellent test for nitrites. Nitrites were also found in the blood and various organs, but in special abundance in the liver. In this connection it is interesting to note that Abelous and Gérard[1] found aqueous extracts of the liver and other organs of the horse to reduce nitrates to nitrites.

It is apparent, therefore, from these results that hyponitrous acid is oxidized to nitric acid in the animal organism. The fact that sodium hyponitrite escaped oxidation under similar conditions is probably to be explained by the fact that this salt is readily decomposed in aqueous solution into caustic soda and nitrous oxide. Then again, it seems to have been pretty well established that salts are more difficult to oxidize than the corresponding acid. It is further evident from our results that nitrous acid and nitrites are partially oxidized to nitrates in the body of higher animals, and also that nitric acid and nitrates are partially reduced to nitrites.[2] We have also observed that aqueous extracts of certain portions of some of the higher plants have also the power of

[1] Compt. rend., **129**, 56–58, 164–166 (1899).

[2] According to some writers the fate of nitrates in the body is somewhat uncertain. According to Weyl, in man the administration of 1 to 3 grams, by the mouth caused no increase in the amount of nitrate in the urine. It was supposed that the nitrate was completely reduced to ammonia or that it was finally excreted by the lungs as free nitrogen. Weyl's results have not been altogether confirmed by other observers and it is certain that when injected subcutaneously into lower animals the nitrate of the urine is greatly increased at the same time that some of it is reduced to nitrite and possibly to ammonia. (Virchow's Arch., **96**, 462, etc.)

changing nitrate to nitrite. Similar results have recently been obtained by Pozzi-Escot[1] in his study of the reductases. It would seem, therefore, that the power to effect those changes ordinarily included under the head of nitrification and denitrification is not confined to a comparatively few micro-organisms, but that these changes can be accomplished, less rapidly perhaps yet none the less certainly, by many if not by all of the higher life-forms. In their general bearing on oxidation and reduction phenomena in the organism our results have still a further significance. The fact that the higher animal can oxidize a nitrite and also reduce a nitrate would seem to indicate that oxidation and reduction processes in the organism tend towards the production and maintenance of a chemical equilibrium. That such is the case is seen not only in the conduct of nitrites and nitrates in the organism but also in the conduct of such compounds as aldehydes. We know now from the researches of Schmiedeberg,[2] Pohl,[3] Medwedew,[4] and Jacoby[5] that aldehydes, such as salicylic, benzoic, and formic aldehyde, are oxidized in the animal organism and also by the extracts of several organs, notably the liver, to the corresponding acid. On the other hand, that these substances are sometimes reduced in the organism is rendered evident by the fact that urochloral acid, a conjugation-product of trichlorethyl alcohol and glycuronic acid, appears in the urine after the administration of chloral. Evidently, therefore, chloral is reduced in the organism to trichlorethyl alcohol. Whether any of it is oxidized in the animal organism seems not to have been determined. The reason for this, however, is not far to seek. In the first place, there are no very delicate tests for its oxidation-product, trichloracetic acid, and in the second place, the salts of trichloracetic acid are readily decomposed in aqueous solution into chloroform and the bicarbonate of the metal,[6] so that it is more than likely that any trichloracetic acid resulting from the oxidation of the chloral

[1] This JOURNAL, 29, 536–541.
[2] Arch. Exp. Path., 14, 288–379.
[3] *Ibid.*, 14, 38–65.
[4] Pflüger's Arch., 65, 249,
[5] Virchow's Arch., 157, 235.
[6] Ber. d. chem. Ges., 18, 3336–3339.

would escape observation on this account.   The decomposi-
tion of sodium formate into hydrogen and sodium bicarbonate
by certain bacteria is a well-known instance of a biochemical
reaction of this order.[1]   Be all this as it may, we know that
outside of the body chloral conducts itself like other alde-
hydes towards oxidizing agents and that, like all bodies of this
class, it is a powerful reducing agent.   We should, therefore,
certainly expect the oxidation of this compound in the animal
body as well as its reduction.   Whether we shall ever be able
to obtain experimental evidence of the products of its oxida-
tion remains to be seen.   Looking at oxidation and reduction
processes in the organism from the standpoint of chemical
equilibrium, it would seem that in the body of warm-blooded
animals aldehydes would be simultaneously oxidized and re-
duced.   This would account for the fact that in some cases
acids, in other cases alcohols, have resulted from the intro-
duction of aldehydes into the organism.   If the first product
of the oxidation is stable it, or some derivative thereof, will
appear in the urine.   Hence, as has been shown by Pohl,[2]
formic acid appears in the urine when formic aldehyde has
been administered to an animal.   Or the first product of the
oxidation of the aldehyde may be still further oxidized.   For
example, Pohl believes that formic acid is partly oxidized in
the body to carbon dioxide and water.   At the same time,
however, that these oxidations are occurring, the reduction
of the aldehyde is also being brought about, and in some in-
stances at least the product of the reduction, an alcohol, or a
conjugation-product thereof appears in the urine.   Thus we
observe that the appearance of urochloral acid follows the ad-
ministration of chloral.   On the other hand, if the alcohol re-
sulting from the reduction of the aldehyde or its conjugation-
product be not removed from the organism, it may also grad-
ually suffer oxidation, and ultimately perhaps take the form
of carbon dioxide and water.   This would satisfactorily ac-
count for the very slow elimination of such substances as
methyl alcohol from the body and would explain the apparent
difficulty with which this substance is oxidized in the organ-

[1] J. Chem. Soc., Trans., **79**, 386 (1901).
[2] For a résumé of Pohl's work see Reid Hunt : '' Toxicity of Methyl Alcohol,''
Johns Hopkins Hospital Bulletin, **13**, Nos. 137, 138.

ism. The tendency on the part of alcohols to react with fatty acids under the influence of lipase to form ethereal salts would also tend to retard the elimination of alcohol by the organism. In this connection Blyth[1] mentions the remarkable attraction which some tissues, notably the brain, have for ethyl alcohol.

The Toxic Action of Powerful Oxidizing and Reducing Substances.

On account of their great diversity in composition and mode of action it has proven extremely difficult to formulate a purely chemical theory of the action of poisons. The nearest approach to a general theory is that of Loew, according to which all substances which enter into combination with aldehyde and ketone groups are poisonous to life. According to this observer the labile proteid groups in protoplasm contain such aldehyde or ketone groups. In connection with our study of the conduct of hyponitrites, nitrites, and nitrates in the organism, we have come to be impressed with the large number of powerful oxidizing and reducing substances which act as poisons. The number of reducing substances, especially, which possess toxic properties, is indeed remarkable. The following may serve as examples of such compounds. The list of such might easily be extended :

Toxic oxidizing compounds.	Toxic reducing substances.
Nitrates	Nitrites
Chlorates	Hydrogen sulphide
Arsenates	Arsenites
Nitrobenzene	Aniline
Picric acid	Phosphorus
Chromates	Phosphine
Organic peroxides and per-acids	Hydroxylamine
	Phenylhydrazine
	Benzene, toluene, turpentine, and other hydrocarbons
	Formic, acetic, and other aldehydes
	Methyl, ethyl, amyl, and other alcohols
	Pyrocatechol, resorcinol, hydroquinol, pyrogallol, etc.

[1] Blyth's " Poisons," Third Edition, p. 140.

No oxidizing compound has been included in the above list but such as is known to be reduced in the organism, and no reducing substance but such as is known to undergo oxidation in the body.

It is interesting to note in this connection that Binz and Schulz[1] have advanced the idea that the protoplasm of many tissues has the power to oxidize arsenious to arsenic acid and also the power to reduce arsenic acid to arsenious, as the result of which the cells are decomposed, fatty degeneration taking place. In this manner they account for the poisonous action of arsenic. It is not intended to convey by the ideas here advanced that the reducing or oxidizing power of a substance is the only property which determines its action as a poison, but rather that all oxidizing and reducing substances have at least one toxic property in common, *viz.*, that they upset the normal respiratory exchanges which occur in the organism, and thereby give rise to a series of disturbances, which may ultimately result in death. It is doubtful, for example, if all of the distressing symptoms which follow the administration of sodium nitrite can be ascribed solely to its action as a reducing agent. On the other hand, it certainly seems reasonable to conclude that this is an important element in its toxic effect, and that anything which like this substance so profoundly alters the oxyhaemoglobin of the blood must, regardless of its particular chemical constitution and specific effects, act as a poison. It is interesting to note in this connection that pharmacologists, among them Cushny,[2] look upon iodates as more poisonous than bromates, and bromates as more poisonous than chlorates. Now Rabuteau[3] has shown that iodates are completely reduced in the body, whereas bromates are reduced only to a slight extent and chlorates not at all. Later, Binz[4] found that potassium chlorate is rapidly reduced at body temperature by pus, yeast, fibrin, etc., so that it is more than probable that at least small

[1] Arch. Exp. Path. u. Pharm., **11**, 131, 200; **13**, 256; **14**, 345; **15**, 322; **36**, 275; **38**, 259; **41**, 179.
[2] Cushny's "Pharmacology and Therapeutics," Third Edition, p. 529.
[3] Compt. rend., **74**, 57.
[4] N. Rep. Pharm., **22**, 733.

amounts of even the chlorate are reduced in the organism. It would seem, therefore, that among a series of analogous compounds the toxicity and power to effect oxidation stand in the same order.

In order to form some idea of the relative toxicity of sodium nitrite and hydroxylamine the following experiments on the rabbit were carried out.

Experiment 14, with N/2 Hydroxylamine Hydrochloride.—A rabbit weighing about 1 kilogram was injected with 3 cc. of a N/2 solution of Kahlbaum's pure hydroxylamine hydrochloride. The animal died twenty minutes after the injection. The internal organs were removed from the animal and placed in water under antiseptic conditions. No nitrite was found in the bladder, kidneys, liver, or heart, but by reducing with zinc dust and then testing with Griess' reagent nitrite was found in all of these organs, thereby indicating of course that all of them contained nitrate. Some of the blood also was dialyzed and found to contain both nitrite and nitrate,[1] the latter in much the larger quantity.

Experiment 15, with N/3 Hydroxylamine Hydrochloride.—A rabbit weighing 1100 grams was injected with 3 cc. N/3 hydroxylamine hydrochloride. The urine from this animal after the injection was found to contain nitrate but no nitrite. The animal died thirty hours after the injection.

Experiment 16, with N/5 Hydroxylamine Hydrochloride.—A rabbit weighing 1 kilogram was injected with 3 cc. N/5 hydroxylamine hydrochloride. The urine passed after the injection was found to contain nitrate and a trace of nitrite. No toxic effects were noted from this amount of the substance and the animal remained healthy as long as under observation.

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[1] In this connection it should be observed that Raimondi and Bertoni (Gazzetta, 12, 195, 198, and 199–203) found that nitrites were present in the blood of animals after poisoning with hydroxylamine, and they have explained the poisonous action of hydroxylamine as really due to the nitrite resulting from it by oxidation. We also found nitrite in the blood of rabbits poisoned with hydroxylamine, but we have found considerably more nitrate than nitrite in the blood, tissues, and urine of such animals. We cannot, therefore, look upon the oxidation of hydroxylamine in the organism as stopping at the nitrite stage. The fact that sodium nitrite is itself oxidized in the organism to nitrate indicates that this cannot be the case.

Experiment 17, with N/3 Hydroxylamine.—A N/3 solution of hydroxylamine, the free base, was prepared by treating the hydrochloride with the required amount of caustic soda. A rabbit weighing a little over a kilogram was injected with 3 cc. of this solution. The urine obtained two hours after the injection was found to be slightly alkaline and to contain small amounts of nitrate but no nitrite. The animal died two days after the injection from the effects of the poison.

It will be seen from our results on sodium nitrite that 3 cc. of a normal solution of this compound, per kilogram body weight, was sufficient to kill a rabbit in thirty minutes, whereas 3 cc. of a half-normal solution of this salt had apparently no harmful effect, or at any rate the animal entirely recovered. The lethal dose of sodium nitrite, therefore, is not far from 3 cc. of the normal solution per kilogram body weight. On the other hand, from our results with hydroxylamine it would seem that 3 cc. of the N/3 solution represents the minimum lethal dose for the rabbit, per kilogram body weight. It would seem, therefore, that of two reducing agents that is the more toxic which possesses the greater capacity for oxygen, and in this connection it is interesting to note that in order to pass to nitrate, hydroxylamine requires three times as much oxygen as is required by sodium nitrite.

In conclusion, it is interesting to note that a great many pathogenic organisms are either anaerobic or facultative anaerobic, and that the growth of bacteria in an impoverished oxygen supply often results in the development of toxines. It has been shown further that diphtheria toxine is rapidly modified by air and sunlight, and that in the absence of air the diminution in toxic activity brought about by sunlight is comparatively slight.[1] It has also been observed by Pasteur[2] that on exposure to air cultures of the anthrax bacillus and the micrococcus of fowl cholera show a gradual loss of pathogenic power. This loss is, according to him, due to the action of oxygen. These and many other facts of kindred nature seem to indicate that lack of oxygen is favorable to the production of

[1] See also Woodhead's " Bacteria and Their Products," p. 141.

[2] Sternberg's " Bacteriology," p. 168.

poisonous compounds by the organism and that probably the
toxines themselves belong to the class of reducing poisons.

STATE COLLEGE OF KENTUCKY,
  LEXINGTON, Sept., 1903.

ON THE PREPARATION OF FORMIMINOETHYL ETHER.[1]

BY H. B. HILL AND O. F. BLACK.

The formiminoethyl ether, $NHCHOC_2H_5$, has become a re-
agent of some importance on account of its use in Claisen's
process for making acetals,[2] but the only method of preparing
it was that of its discoverer, Pinner,[3] which consisted in shak-
ing a mixture of anhydrous prussic acid and absolute alcohol
in the proportion of 1 molecule of each, diluted with absolute
ether, with a little more than a molecule of hydrochloric acid
gas in a freezing-mixture. This process is certainly unde-
sirable because of the large quantity of anhydrous prussic
acid which must be used, and also since it requires very care-
ful manipulation and regulation of the temperature to prevent
dangerous explosions.

In the hope of removing these disadvantages we have sub-
stituted mercuric cyanide for the prussic acid and have found
that in this way a yield of 84 per cent of the double salt,

$$HClHNCHOC_2H_5HgCl_2,$$

can be obtained without difficulty, so that the preparation of
the formiminoethyl ether becomes a simple and convenient
operation. The details of the process follow :

Twenty grams of finely powdered mercuric cyanide and
21.6 grams of mercuric chloride were mixed in an Erlenmeyer
flask with 7.3 grams of absolute alcohol diluted with several
times its volume of absolute ether. The proportions give 2
molecules of the alcohol to each molecule of the cyanide.
The flask was then immersed in ice-water and treated with
dry hydrochloric acid gas, with frequent shaking, until the

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[1] The work described in this paper was done under the supervision of Professor
Hill, but the paper was written after his untimely death.   C. L. J.

[2] Ber. d. chem. Ges., **31**, 1010.

[3] *Ibid.*, **16**, 354.

mercuric cyanide had gone into solution and the liquid fumed strongly. The mixture was then allowed to stand for half an hour, during which time the double salt crystallized out in colorless plates. These were filtered out on the pump and washed several times with anhydrous ether. The yield from 20 grams of mercuric cyanide was 51 grams of the crystalline salt, amounting to 84 per cent of that required by the theory, if all the cyanogen was converted into the salt. The double salt is comparatively stable and its formation was attended with no perceptible evolution of hydrocyanic acid.

A sample of the salt dried *in vacuo* over potassic hydrate and sulphuric acid gave the following results on analysis :

I. 0.5022 gram substance gave, on combustion, 0.1723 gram CO_2 and 0.0944 gram H_2O.

II. 0.4913 gram salt gave, by the Carius method, 0.5572 gram AgCl.

III. 0.4312 gram substance gave 0.4888 gram AgCl.

IV. 0.3082 gram substance gave 0.1880 gram HgS.

V. 0.3177 gram substance gave 0.1947 gram HgS.

	Calculated for $C_3H_8NOCl_3Hg$.	I.	II.	Found. III.	IV.	V.
C	9.46	9.35	....	....	....	....
H	2.10	2.09	....	....	....	....
Cl	27.99	....	28.04	28.02	....	....
Hg	52.55	....	....	....	52.58	52.82

The formula of the substance is therefore

$$HClHNCHOC_2H_5HgCl_2.$$
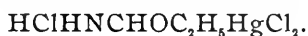
To prove that the substance is a salt of the formiminoethyl ether some of it was suspended in absolute ether and mixed with aniline, when a precipitate, probably a double chloride of mercury and aniline, was formed. The ethereal filtrate from this deposited, on evaporation, light-yellow needles, which, on recrystallization from dilute alcohol, melted at 135° to 137°, showing that they were the diphenylformaniline prepared by Pinner[1] by the action of aniline on the formiminoethyl ether.

It still remained to be proved that this mercuric salt could

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[1] Ber. d. chem. Ges., **16**, 358.

take the place of the chloride of formimino ether in Claisen's reaction. Accordingly, the following experiment was made : Fifty grams of the mercury salt of formiminoethyl ether were dissolved in absolute alcohol, using a little more than 2 molecules of alcohol to each molecule of the salt. In a short time the solution became full of white, silky needles, which were finally deposited in such quantity that the whole set to a hard mass. This, after standing for several days, was extracted with absolute ether and the extract submitted to fractional distillation. In this way 7.5 grams of a liquid were obtained, boiling at 145° to 147°, and therefore orthoformic ethyl ether, $HC(OC_2H_5)_3$. This reaction shows that the salt can be used in place of the chloride in preparing acetals according to Claisen's method, since this depends on the formation of nascent orthoformic ether. The secondary product from the formation of the orthoformic ether was proved to be the double chloride of mercury and ammonium by the following analyses :

I. 0.3027 gram substance gave 0.2173 gram HgS.

II. 0.3022 gram substance gave 0.2160 gram HgS.

III. 0.3007 gram substance gave 0.4027 gram AgCl.

	Calculated for NH_4HgCl_3.	I.	Found. II.	III.
Hg	61.66	61.88	61.61	....
Cl	32.84	....	....	33.11

Zincic cyanide gave, when heated in the same way as the mercuric cyanide, a zinc double salt of the chloride of formiminoethyl ether, but, as it is very deliquescent, the mercury salt is to be preferred for practical purposes. Argentic cyanide, or potassic cyanide, yielded no result.


THE ACTION OF BROMINE ON 2,6-DIBROMPARA-PHENYLENEDIAMINE.

BY C. LORING JACKSON AND D. F. CALHANE.

The object of this research was to make a more careful study of the conversion of paraphenylenediamines into quinones, and, as we hoped that the intermediate products might be more stable if the benzol ring was loaded with atoms of

bromine, we first tried to make the tetrabromparaphenylene-
diamine, a substance prepared some years ago in this labora-
tory but not as yet described. For this purpose we dissolved
some of the 2,6-dibromparaphenylenediamine in absolute
ether and treated it with bromine also diluted with ether, but
the reaction did not run as we had expected, for instead of a
slightly colored substitution-product we obtained a dark but
vivid green precipitate, which seems to be one of the products
intermediate between the diamine and the quinone, of which
we were in search. The analysis of this substance, which
looks much like a good specimen of chromic oxide, gave num-
bers corresponding to the formula $C_6H_2Br_2(NH)_2HBr$, and
that it was a bromide was shown by the action of an aqueous
solution of sodic carbonate, which set free a base dissolving
in ether with a blood-red color, with the formation of the cal-
culated amount of sodic bromide. The red solution of the
base was also obtained by shaking the green bromide with
ether and ammonia gas, or an amine. Such a solution gave,
with hydrobromic acid gas or hydrochloric acid gas, a green
precipitate exactly like the original. The chloride contained
an amount of chlorine corresponding to $C_6H_2Br_2(NH)_2HCl$.

The percentage composition of the diimine is so near to that
of the diamine that it was possible a considerable amount of
the bromide of the latter might be mixed with the colored
salt, and to settle this point the preparation of the green salt
was carried on quantitatively, when it was found that the
amount of bromine used corresponded to 1 molecule of bro-
mine to 2 molecules of the 2,6-dibromparaphenylenediamine.
It follows therefore that the action is most simply expressed
by this reaction,

$$2C_6H_2Br_2(NH_2)_2 + Br_2 =$$
$$C_6H_2Br_2(NH)_2HBr + C_6H_2Br_2(NH_2)_2HBr,$$
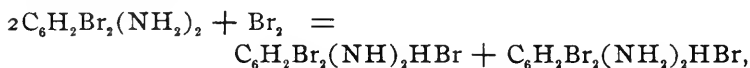
and that about one-half of the green precipitate consists of
the bromide of the diamine. That this reaction did not run
perfectly smoothly was shown by the fact that the filtrate in
these quantitative experiments was colored red probably by
some of the free diimine. We have not as yet obtained either

the diimine or its salt free from this impurity of diamine, because our work has been much retarded by the pressure of other duties. Our reason for publishing the paper in this unfinished state is that we cannot continue the work together owing to the departure of one of us from Cambridge.

The arguments in favor of considering the colored base, the diimine, $C_6H_2Br_2(NH)_2$, are, that the formula explains simply the formation of the substance from bromine and the diamine, and also the color and slight stability of the compound. We are aware that these arguments are not convincing, but were prevented for the reason already given from furnishing an experimental proof of its structure. We had, in fact, tried several experiments with reducing agents on the salt, but we prefer not to publish these until further work in this direction has led to definite results. In the absence of these we adopt, provisionally, the theory that our new substance is a diimine.

The free base is so unstable that we did not succeed in purifying it for analysis, or in making the acetyl or benzoyl derivative. It decomposes quickly into a brown substance dissolving in ether with a brown color. This part of the subject will also be studied more carefully in the coming year.

That this colored base is a step in the conversion of diamines into quinones seems evident from the facts that the 2,6-dibromparaphenylenediamine is converted into 2,6-dibromquinone by treating it with bromine and water, and that the colored salt gives the same product with the same reagents.

Paraphenylenediamine, when treated with bromine in anhydrous ether, gives a similar precipitate of a somewhat brighter blue than Prussian blue, which, on analysis, gave results agreeing fairly well with the formula $C_6H_4(NH)_2HBr$. This blue precipitate was undoubtedly contaminated with some of the green $C_6H_2Br_2(NH)_2HBr$, as an excess of bromine converted the blue product into this green salt, but our analytical data are near enough to show that the first action of the bromine consists in the modification of the amino groups and not in the replacement of the hydrogen of the benzoyl ring. This blue salt also undoubtedly contains a large quantity of

the bromide of paraphenylenediamine. It is more stable than the green salt, as it is less decomposed by water or alcohols, which is probably due to the fact that the basic properties of the diimine are not neutralized by the presence of bromine in the ring here, as they are in the green $C_6H_2Br_2(NH)_2HBr$. Orthophenylenediamine gives, under the same conditions, a colored precipitate similar to that from the paradiamine, but much less stable. Metaphenylenediamine, on the other hand, when treated with bromine in anhydrous ether, gives only a white precipitate, undoubtedly a substitution-product.

Hencke[1] obtained a substance which seems to belong to the same class as our so-called diimines, by the action of plumbic dioxide on paraminodiphenylamine, $NH_2C_6H_4NHC_6H_5$, in ethereal solution. The product gave results on analysis corresponding to the formula $C_6H_4NHNC_6H_5$, had a brown color, and gave a bluish-green color with glacial acetic acid. Hencke, however, thinks that it is not a simple diimine, but has a higher molecular weight.

For the sake of comparison in our attempts to make the benzoyldiimine we were obliged to make the monobenzoyl-2,6-dibromparaphenylenediamine,

$$C_6H_2Br_2NH_2NHCOC_6H_5,$$
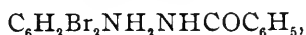
which melts at 194°.

All the colored substances mentioned above will be submitted to a more careful study during the coming year in this laboratory, and attempts will be made to prepare other substances of the same class.

<div style="text-align:center">EXPERIMENTAL PART.</div>

Action of Bromine upon 2,6-Dibromparaphenylenediamine in Absolute Ether.

The 2,6-dibromparaphenylenediamine used in this work was prepared from paranitraniline, which was dissolved in strong hydrochloric acid by the aid of heat, the solution diluted with water to a volume of about 5 liters, and treated with a stream of air saturated with bromine vapor until the liquid showed a permanent red color. The precipitate of dibromni-

[1] Ann. Chem. (Liebig), **255**, 193 (1889).

traniline thus obtained was next reduced to the dibrompara-phenylenediamine with tin and hydrochloric acid. It was found convenient to use not more than 25 grams in each reduction, and in this case the action was complete after heating in a flask on the steam-bath for four or five hours. Two methods were used in working up the product of the reduction, neither of which, however, gave a satisfactory yield. The simplest method consisted in precipitating the diamine with sodic hydrate, which was not added in sufficient amount to redissolve completely the hydrates of tin, the precipitate was filtered out, dried, powdered, and extracted with a boiling mixture of equal volumes of ligroin and benzol. In the second method the liquid poured off from undissolved tin was allowed to stand in a cool place until the double tin salt had separated. This was filtered out, washed with cold water, dissolved in hot water, and saturated with sulphuretted hydrogen. The filtrate from the sulphide of tin was rendered strongly alkaline with sodic hydrate, this being added in sufficient quantity to redissolve any hydrate of tin present, and then extracted with ether in a continuous extractor.

The anhydrous ether used in these experiments was prepared by shaking common ether two or three times with water, drying it for twenty-four hours over calcic chloride, for twenty-four hours over sodium, and distilling over sodium. Two grams of the 2,6-dibromparaphenylenediamine were dissolved in 100 cc. of this anhydrous ether, and 0.2 cc. of bromine was also dissolved in 100 cc. of the ether. After both solutions had been cooled with ice, they were mixed, when a heavy green precipitate was formed, which was filtered out, washed with anhydrous ether, dried *in vacuo*, and analyzed with the following results :

I. 0.1572 gram substance gave, by the Carius method, 0.2562 gram AgBr.

II. 0.1974 gram substance gave 0.3196 gram AgBr.

III. 0.3594 gram substance gave 24.3 cc. moist N_2 at 28° and 765 mm. pressure.

IV. 0.2372 gram substance gave 18 cc. moist N_2 at 17° and 768 mm. pressure.

V. 0.4822 gram substance gave, on combustion, 0.3752 gram CO_2 and 0.1146 gram H_2O.

	Calculated for $C_6H_2Br_2(NH)_2HBr.$	I.	II.	Found. III.	IV.	V.
Br	69.56	69.33	68.89	....	....	....
N	8.12	....	....	7.47	8.90	....
C	20.86	....	....	....	....	21.22
H	1.45	....	....	....	....	2.64

As most of these analyses were made with specimens from different preparations, there is no doubt that the precipitate has a constant composition.

The results of the combustion are not so near to the percentages required by the formula as we could wish, but, as hydrobromic acid is given off rapidly by this easily decomposed substance, we could hardly expect better results. A specially long porcelain boat was used, and the substance was mixed in it with a quantity of a mixture of 8 parts of plumbic chromate and 1 part of potassic dichromate. Plumbic chromate also replaced almost all the cupric oxide in the tube.

The results obtained seemed to indicate that the substance is the bromide of the 2,6-dibromparaphenylenediamine.

Two grams of the diamine gave from 1.8 to 1.95 grams of diimine bromide, whereas the theory requires 2.59 grams. The yield, therefore, was 75 per cent of that demanded by the theory.

Another confirmation of this theory of the nature of our compound was given by its behavior with sodic carbonate, which converted it into a brownish-red substance with the formation of sodic bromide. The amount of bromine removed was determined as follows :

0.5226 gram green salt gave, after decomposition with an aqueous solution of pure sodic carbonate, 0.2830 gram $AgBr$.

	Calculated for $C_6H_2Br_2(NH)_2HBr.$	Found.
Br	23.19	23.45

It is hardly possible that this reaction can be other than the conversion of a salt into the corresponding free base.

To settle this point more completely the following experiment was tried : One-tenth gram of isoamylamine was dis-

solved in 25 cc. of anhydrous ether, and 0.5 gram of the green salt was added to this solution in small portions at a time, shaking the mixture thoroughly after each addition. The mixture was allowed to stand five minutes and then filtered from isoamylamine bromide into a test-tube containing 30 cc. of dry ether, 5 cc. of which had been saturated with hydrochloric acid gas. The blood-red filtrate, as soon as it came in contact with the hydrochloric acid, formed a deep-green precipitate, which could not be distinguished by the eye from the original bromide. This was washed thoroughly with ether, dried, and the amount of chlorine removed from it by aqueous sodic carbonate determined as follows:

0.1935 gram substance gave 0.0887 gram AgCl.

	Calculated for $C_6H_2Br_2(NH)_2HCl$.	Found.
Cl	11.81	11.31

These results leave no doubt that we have here a red base, which forms a green bromide or chloride, but they do not prove that the substance is pure, as the analyses cannot determine between the salt of a diimine and a diamine, and in fact the work next to be described showed that the green precipitate was a mixture containing a considerable quantity of the bromide of the diamine mixed with the colored salt. The object of these experiments was to trace quantitatively the formation of the green bromide. This was done by the use of a standard solution of bromine in anhydrous ether, which was added to the ethereal solution of the 2,6-dibromparaphenylenediamine until a drop acted on a potassic iodide and starch paste paper.

At first we tried the action of undiluted bromine on the ethereal solution of the diamine, but found that the reaction was too violent. A solution of bromine in chloroform also gave bad results, as shown by the dirty color of the precipitate. We were obliged, therefore, to use a solution of bromine in anhydrous ether, and succeeded in getting good results, if the solutions were used as soon as they were made, since they deteriorate rapidly from the substituting action of the bromine on the ether.

I. A solution of bromine in anhydrous ether, containing 0.006 gram of bromine in each cubic centimeter, was used. Five-tenths gram of the 2,6-dibromparaphenylenediamine were dissolved in anhydrous ether, and to this was added a mixture of 25 cc. of the solution of bromine diluted with its own volume of ether. The titration was then finished by adding the solution of bromine from a burette ; 26 cc. of the solution of bromine were needed.

II. The solution used contained 0.015 gram in the cubic centimeter. Five-tenths gram of the 2,6-dibromparaphenylenediamine dissolved in anhydrous ether required 10 cc. of this solution.

	Calculated for		Found.	
	$C_6H_2Br_2(NH_2)_2$.	$2C_6H_2Br_2(NH_2)_2$.	I.	II.
Br	0.3007	0.1504	0.1560	0.1500

Under the heading ''calculated'' the amount of bromine in grams is given, which would be used if 1 molecule of bromine acted on 1 or 2 molecules of the diamine. The results show that each molecule of bromine acted on two of the 2,6-dibromparaphenylenediamine instead of on one, as would be the case if the green precipitate were the pure salt of the diimine. If, then, the diimine is really formed, the reaction runs as follows :

$$2C_6H_2Br_2(NH_2)_2 + Br_2 =$$
$$C_6H_2Br_2(NH)_2HBr + C_6H_2Br_2(NH_2)_2HBr,$$
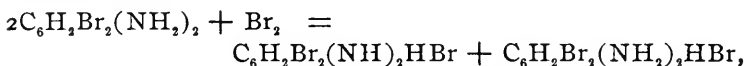
and the product is a mixture of the bromides of the diamine and diimine. This view is supported by the fact that the ethereal filtrate from the green precipitate contained no hydrobromic acid. It had, however, a strong red color, which indicated that it contained some of the diimine and that the reaction did not run with perfect smoothness.

In the preceding discussion we have called our colored product the diimine, but the data at our disposal are not sufficient to establish its nature with certainty, and we feel it will be wiser to postpone all description of the reduction-experiments undertaken for this purpose until they have led to some definite result.

Properties of the Bromide of 2,6-Dibromparaphenylenedi-imine(?).—The specimens prepared by us all contained a considerable proportion of the bromide of the diamine, but the properties given here are such that the presence of this impurity would not interfere with them. It forms a dark but vivid green powder, looking like a fine specimen of chromic oxide. Water changes its color from green to purplish-black. Alcohol turns it red, probably from the formation of the free base. This decomposition is more rapid when the alcohol is hot, much less rapid when absolute alcohol is used instead of common alcohol. Chloroform seems to have no action on it in the cold, but decomposes it slowly when boiling. Isoamyl alcohol is colored red by it, showing apparently the formation of the free base. Strong hydrochloric acid dissolves it with a deep purplish color, and the diluted solution deposits, on standing, a dark purple, flocculent precipitate. Sodic carbonate in aqueous solution decomposes it, forming a brown precipitate of the free base. This reaction was used in the analysis of the substance. The free base thus formed dissolves, if fresh, in ether, benzol, or acetone with a blood-red color. The red solution is most conveniently obtained by treating the bromide suspended in anhydrous ether with gaseous ammonia or an amine. That it was the base was shown by treating its ethereal solution with gaseous hydrobromic acid or hydrochloric acid, when a green precipitate of the bromide or chloride was formed. The chloride could not be distinguished by the eye from the bromide. The free base was very unstable, passing in a very short time into a substance which gave a brown solution in ether. All our attempts to obtain the free base in a pure state for analysis, or to make its benzoyl, or acetyl derivative failed, but these experiments will be resumed in the coming year in this laboratory, and its brown decomposition-product will also be studied.

Action of Bromine on Paraphenylenediamine in Ethereal Solution.

Six-tenths of a gram of paraphenylenediamine were dissolved in 250 cc. of anhydrous ether and cooled thoroughly

with ice. To this solution was added a mixture of 0.15 cc. of bromine and 75 cc. of anhydrous ether, also cooled with ice, when a brilliant blue precipitate was obtained, which yielded the following results on analysis :

I. 0.2464 gram substance gave, by treatment with sodic carbonate in aqueous solution, 0.2410 gram AgBr.

II. 0.2348 gram substance gave 0.2292 gram AgBr.

	Calculated for $C_6H_4(NH)_2HBr$.	Found. I.	II.
Br	42.79	41.63	41.55

0.3105 gram substance gave, by the Carius method, 0.3401 gram AgBr.

	Calculated for $C_6H_4(NH)_2HBr$.	Found.
Br	42.79	46.60

These results leave much to be desired, but are explained by the fact that an excess of bromine acts upon the blue substance converting it into the green 2,6-dibromparaphenylenediimine bromide just described, as we proved by a special experiment. It was hardly to be expected, therefore, that we should get the blue precipitate entirely free from the green one containing more bromine. Our analyses, although so imperfect, are given, because they show that the action of the bromine is exerted on the amino groups before it begins to replace the hydrogen of the ring.

Properties of the Bromide of Paraphenylenediimine(?).—The preparation undoubtedly contained a large proportion of the bromide of the diamine. It forms a dark blue powder looking like Prussian blue, but rather lighter in color. It is more stable than the green dibrom compound, and it is sparingly soluble in water, apparently without decomposition. It is also more stable toward alcohol, in which it dissolves with the formation of only a slight red color. Chloroform does not decompose it apparently, even when hot. Cold isoamyl alcohol dissolves it without change of color, but, when the solution is boiled, it turns red.

Orthophenylenediamine, when treated with bromine in anhydrous ether, also gave a colored precipitate, which was far

less stable than that formed from the paradiamine. Meta-phenylenediamine, under these conditions, gave a white precipitate, obviously a substitution-product.

Monobenzoyl-2,6-dibromparaphenylenediamine,
$C_6H_2Br_2NH_2NHCOC_6H_5$.—This substance was made in order to compare it with the products obtained by the action of benzoyl chloride on our red base. As we cannot find that it has been described, we give an account of it.

Two grams of 2,6-dibromparaphenylenediamine were dissolved in 100 cc. of ether, and the calculated amount of benzoyl chloride, diluted with ether, added. The copious white precipitate thus formed was filtered off, washed with water, dried, and recrystallized from dilute alcohol until it showed the constant melting-point 194°, when it was dried *in vacuo* and analyzed with the following result :

0.2303 gram substance gave, by the Carius method, 0.2338 gram AgBr.

	Calculated for $C_6H_2Br_2NH_2NHCOC_6H_5$.	Found.
Br	43.24	43.20

Properties of the Monobenzoyl-2,6-dibromparaphenylenediamine.—It crystallizes in short, creamy-white prisms with a vitreous luster. It melts at 194°, and is soluble in ethyl or methyl alcohol, glacial acetic acid, or acetone ; sparingly soluble in benzol, chloroform, or ligroin ; essentially insoluble in ether. The best solvent for it is dilute alcohol. Strong hydrochloric acid has no apparent action on it, even when hot. Fuming nitric acid dissolves it with a yellow color ; dilution throws down a white precipitate. Strong sulphuric acid dissolves it in the cold.

Action of Bromine and Water on the 2,6-Dibromparaphenylenediamine.

A specimen of the 2,6-dibromparaphenylenediamine was suspended in cold, dilute hydrochloric acid and treated with bromine in the proportion of 2 molecules of bromine to each molecule of the diamine. The yellow product formed was purified by crystallization from ligroin, when it gave broad,

yellow plates, melting at 126°. As it seemed evident from this that the substance was the dibromquinone melting at 131°, the purification was not continued. The same product seemed to be formed when the green 2,6-dibromparaphenylene-diimine bromide was treated with bromine and water.

CAMBRIDGE, MASS., October, 1903.

THE SPECIFIC GRAVITIES OF CADMIUM CHLO-RIDE AND CADMIUM BROMIDE.

BY GREGORY PAUL BAXTER AND MURRAY ARNOLD HINES.

Recent investigation in this laboratory upon atomic volume[1] has made it desirable to obtain the densities of certain salts with great accuracy. If a solid is of such a nature that it may be easily obtained in a pure state, the determination of its specific gravity offers no especial difficulties. The "inclusion" of mother-liquor which takes place whenever salts are formed from solution,[2] and the danger of incomplete expulsion of all crystal and "adsorbed" water make the determination of the specific gravity of a salt a more or less uncertain process, unless precautions are taken to avoid these pitfalls. In the case of the halogen salts of cadmium, the tendency to become basic when they are heated in a moist condition is an additional source of error. Thus it is not surprising that the values heretofore obtained for the specific gravity of cadmium chloride vary between 3.65 and 3.94,[3] and those for cadmium bromide between 4.71 and 4.91.[4]

In this investigation the method employed for preparing very pure, dry cadmium chloride was that of igniting a double chloride of cadmium and ammonium in a current of hydrochloric acid gas. A salt of the formula $CdCl_2NH_4Cl$ has been described,[5] which for this purpose has the great advantages of containing no water of crystallization, and a small proportion of ammonium chloride.

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[1] Richards : Proc. Am. Acad., **37**, 3, 399; **38**, 293.

[2] Richards : Proc. Am. Phil. Soc., **42**, 28 (1903).

[3] Bödeker : Die Beziehung zwischen Dichte und Zusammenhang bei festen und liquiden Stoffen (1860), 3.625 ; Clarke : Am. J. Sci., [3], **16**, 202 (1878), 3.938 at 23°; Clarke : This JOURNAL, **5**, 240 (1883), 3.655 at 17°.

[4] Clarke : This JOURNAL, **5**, 240 (1883), 4.794 at 20°; Bödeker : *Loc. cit.*, 4.712–4.91.

[5] Rimbach : Ber. d. chem. Ges., **30**, 3073 (1897).

A quantity of the double salt was prepared by dissolving cadmium and ammonium chlorides in the above proportions and evaporating the solution to the point of crystallization. The crystals were separated from the mother-liquor, recrystallized several times from pure water, dried between filter-papers, and exposed to the air for a short time.   In order to make certain that the crystals possessed the desired composition, analysis of the air-dried salt was carried out as follows : A weighed sample of the double chloride was dissolved in water and the chlorine determined in the usual way by precipitation with silver nitrate.   The ammonia was estimated by decomposing the salt with sodium hydroxide and distilling into standard acid.   Finally, to determine the cadmium, a known amount of the salt was dissolved in an excess of potassium cyanide and the solution was electrolyzed in a weighed platinum crucible.

	Calculated for $CdCl_2NH_4Cl$.	Found.
Cl	44.97	44.88
		44.82
NH_4	7.60	7.60
		7.67
Cd	47.42	47.26
		47.48

The composition of our salt is evidently that already cited.
In order to show that ignition of the double salt would give pure cadmium chloride, portions of the salt, contained in a platinum boat, were heated in a tube of hard glass in a current of hydrochloric acid gas, until all sublimation of ammonium chloride ceased.   This acid was generated by dropping concentrated sulphuric acid into concentrated hydrochloric acid, and was dried by means of several columns containing beads moistened with concentrated sulphuric acid, and finally by a tube of phosphoric anhydride which had been sublimed in a rapid current of dry air to get rid of phosphorous impurities. Heating for an hour, at first gently, then with the full heat of two Bunsen burners, in a rapid current of gas, was sufficient to remove the last traces of ammonium chloride.   After the hard glass tube had been allowed to cool, the hydrochloric acid gas

was displaced by pure dry nitrogen[1] and this in turn by dry air. Finally the boat was transferred to a weighing-bottle without an instant's exposure to moisture by the method so frequently used for the purpose in this laboratory.[2]

The apparatus used for the above operations was constructed entirely of glass, except for a few rubber connections in the apparatus for purifying nitrogen and air.[3] Since these latter gases were subsequently conducted over beads moistened with silver nitrate solution, no sulphur compounds could have been introduced from this source. Cadmium chloride prepared in this way gives a clear solution in water, showing that no basic salt is formed in the process. It was easily proved that all ammonium chloride had been expelled by testing the solution with Nessler's reagent, for no appreciable coloration was produced.

The determination of the specific gravity of cadmium chloride was effected with the aid of a pycnometer constructed especially for the purpose. It is a modification of a pycnometer devised by T. W. Richards for the determination of the specific gravity of solids.[4] The weighing-bottle was provided with two glass stoppers, one of which was of ordinary shape and was used during the weighing of the chloride. Into the other were sealed two capillary tubes which served to fill the vessel with liquid. The weighing-bottle and the pycnometer stopper were both made of thick glass in order to avoid distortion when the stopper was inserted.
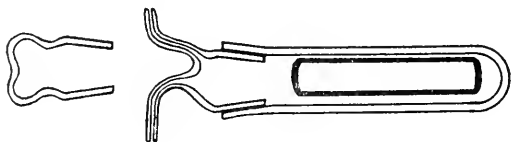
As the bottle was more conveniently made with a round

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[1] Made by passing air through strong ammonia, then over hot copper gauze, and finally removing the excess of ammonia with sulphuric acid.

[2] Richards and Parker : Proc. Am. Acad., **32**, 59.

[3] The apparatus for generating and purifying gases was essentially identical with that used by Richards and Parker in preparing pure magnesium chloride. See Proc. Am. Acad., **32**, 67.

[4] A description of this pycnometer will soon be published.

bottom, a platinum carriage was constructed to hold the bottle on the balance pan. This carriage was used in all weighings of the bottle.

Experiments were first undertaken to determine the accuracy with which the pycnometer could be weighed when filled with a liquid. The pycnometer was immersed as far as possible in water at 25°, and was filled exactly to a mark etched upon one capillary. It was then wiped with a slightly dampened cloth and weighed at intervals of five minutes. It was found that a regular loss in weight of nearly 0.3 milligram per minute took place. Although the stopper was reground with emery dust so that it fitted perfectly, it was found impossible to reduce the loss below 0.2 milligram per minute. This difficulty was caused by leakage of water through the glass joint, owing to capillarity and to its subsequent evaporation. In order to prevent this evaporation, 2 or 3 milligrams of soft paraffin were placed on the upper portion of the ground surface of the stopper before it was inserted in the bottle. The pycnometer, when filled with water as before, then remained absolutely constant in weight.

As cadmium chloride was found to be insoluble in toluol, this liquid was used in the determination of the specific gravity of the salt. Toluol was dried over fused caustic potash and then distilled, the first and last portions being discarded. Its specific gravity at 25° was determined, first with the ordinary form of Ostwald pycnometer, then by the pycnometer which has been described. When the pycnometer was filled with toluol the stopper was made tight with syrupy phosphoric acid. For details concerning the filling of the pycnometer, see page 226.

Ostwald Pycnometer.

Weight of pycnometer.	Weight of pycnometer filled with water.	Weight of pycnometer filled with toluol.	Weight of water.	Weight of toluol.	Density of toluol. 25°/4°.
Grams.	Grams.	Grams.	Grams.	Grams.	
6.9548	15.2431	14.1138	8.2883	7.1590	0.86139

New Pycnometer.

Weight of pycnometer and grease. Grams.	Weight of pycnometer fill'd with water. Grams.	Weight of pycnometer and phosphoric acid. Grams.	Weight of pycnometer fill'd with toluol. Grams.	Weight of water. Grams.	Weight of toluol. Grams.	Density of toluol. 25°/4°.
15.5747	25.0540	15.5749	23.7627	9.4793	8.1878	0.86138

An average of the two values, 0.86138, was used in the calculation of the specific gravities of the salts. The agreement of the results obtained by the two pycnometers shows that the new form of pycnometer is capable of giving accurate results. Nevertheless, a confirmatory test was carried out with some very pure fused silver bromide which resulted from a determination of the atomic weight of iron by one of us.[1] The bromide was fused in a porcelain crucible, cooled, and cut into pieces. Two determinations of the specific gravity of the salt were made by displacing toluol in the new pycnometer and two with the Richards pycnometer. In the calculations a vacuum correction of $+0.000046$ was applied to every apparent gram of silver bromide. No vacuum correction was necessary for the toluol, since the air displaced by the pycnometer filled with toluol was always the same.

Number of determination.	Form of pycnometer.	Weight of AgBr in vacuum. Grams.	Weight of toluol displaced in vacuum. Grams.	Density of AgBr. 25°/4°.
1	New	7.2427	0.9628	6.480
2	"	7.4305	0.9877	6.480
			Average,	6.480
3	Richards	7.0379	0.9361	6.476
4	"	5.0077	0.6660	6.477
			Average,	6.477
		Average of all four determinations,		6.478[2]

[1] Baxter: Proc. Am. Acad., **39**, 245 (1903).

[2] Previous determinations of the density of silver bromide are as follows:

Karsten: J. für Chem. und Physik, **65**, 394 (1831). Precipitated 6.353.

Schröder: Pogg. Ann., **106**, 226 (1859). Precipitated 6.387 to 6.521. Fused 6.315 to 6.428.

Clarke: Am. J. Sci., [3], **13**, 294 (1877). Precipitated 6.215 at 17°.

Rodwell: Phil. Trans., 1882, 1125. 6.245 at 0°.

Less than one-twentieth per cent difference exists between the results obtained by the two pycnometers.   This difference corresponds to an error in weighing the displaced toluol of only about 0.5 milligram.   Evidently our new pycnometer is suitable for the purpose.

Purification of Materials.

Ammonium Chloride.—One kilogram of ammonium chloride was dissolved in water, 100 cc. of concentrated nitric acid were added, and the solution was boiled for several days to destroy the amines.   The salt was then crystallized six times from pure water.   Ammonia was generated from this ammonium chloride by means of sodium hydroxide and was absorbed in pure water.   Ammonia was again evolved by heating the solution of ammonium hydroxide and was collected in pure redistilled hydrochloric acid in a platinum dish.   The resulting ammonium chloride was crystallized once from pure water.

Cadmium.—Five hundred grams of cadmium sulphate were dissolved in about 2.5 liters of water, and 300 cc. of concentrated hydrochloric acid were added to the solution.   Hydrogen sulphide was then passed into the solution to saturation. After the cadmium sulphide thus formed had been thoroughly washed by decantation, it was dissolved in redistilled nitric acid and the cadmium nitrate was crystallized several times from pure water, the last two crystallizations being carried out in platinum vessels.   The nitrate was dissolved in water, enough pure redistilled sulphuric acid to convert the nitrate into the sulphate was added, and the solution was heated on a steam-bath until all the nitric acid was expelled.   An aqueous solution of the sulphate was then electrolyzed, a platinum dish which contained the solution acting as cathode. The deposit consisted of fine crystals, but adhered strongly to the dish and could be washed without difficulty.   Finally the cadmium was dissolved in pure hydrochloric acid, which had been distilled with a platinum condenser into a platinum dish.

In order to prepare the double chloride, the purified ammonium chloride was added to the solution of cadmium chloride in slight excess of the amount required by the formula

$CdCl_2NH_4Cl$. The solution was allowed to stand over pure metallic cadmium for one week and was then evaporated to crystallization. Finally the double salt was recrystallized several times from the purest water in a platinum dish, and the crystals were dried as completely as possible in a vacuum desiccator containing fused potassium hydroxide.

The method of procedure was as follows: The weight of the pycnometer, containing the empty platinum boat and filled with toluol at 25°, was determined twice. From these weights and the weight of the pycnometer and boat alone, the weight of toluol contained by the pycnometer was obtained. In each experiment, after the bottle had been weighed with the salt, the ordinary stopper was removed and sufficient toluol was introduced completely to cover the boat and salt. Then the system was placed in a desiccator which was immediately exhausted by means of a powerful air-pump. Next the pycnometer stopper, which had been weighed with the small amount of syrupy phosphoric acid necessary to make the ground joint tight, was inserted and the pycnometer was filled with toluol exactly to the mark, in a constant temperature-bath. In order to avoid any error from absorption of water by the phosphoric acid, the stopper was inserted immediately after weighing. Finally, the pycnometer was wiped with a slightly dampened cloth and weighed after a few moments' standing in the balance case. From the weight of the system thus obtained, the weight of the salt, and the weight of toluol contained by the pycnometer with the empty boat, was calculated the weight of toluol displaced. The cleansing of the boat in Experiments 4 and 5 caused a loss in weight of a few tenths of a milligram, so that theoretically the toluol content of the pycnometer increased. The weight of toluol displaced by this small quantity of platinum is, however, too minute to be taken into consideration. In the calculations a vacuum correction of $+0.00015$ gram was applied to every apparent gram of cadmium chloride. Needless to say, the gold-plated brass weights were carefully standardized to tenths of a milligram, and the corrections for the thermometer at 0° and 32°.38 were determined.

Number of deter-mination.	Weight of CdCl₂ in vacuum. Grams.	Weight of toluol displaced in vacuum. Gram.	Density of CdCl₂. 25°/4°.
5	2.8842	0.6136	4.049
6	2.1876	0.4660	4.044
7	3.0639	0.6517	4.050
8	0.9821	0.2087	4.054
9	3.1245	0.6647	4.049
		Average,	4.049

In the cooled salt, which was transparent and crystalline, were visible a very few minute bubbles of gas; hence the observed specific gravity is slightly too low. Furthermore, a trace of platinum was visible in some cases. Whether this platinum had its source in the attacking of the boat, or was contained in the original salt, was uncertain. The boat did not perceptibly lose in weight, however, except in the cases when it was subjected to scrubbing with sand during the cleansing. At all events the amount of this platinum was too small to have had an appreciable effect upon the specific gravity.

The specific gravity of cadmium bromide was determined with a sample of salt prepared by O. W. Huntington for use in the determination of the atomic weight of cadmium.[1] The salt was fused in a platinum boat in a current of pure nitrogen and hydrobromic acid gases, and bottled in dry air as previously described. The apparatus for generating hydrobromic acid was that employed by one of us in a determination of the atomic weight of iron,[2] and the purest bromine was used for the purpose. After the salt had been weighed, its specific gravity was determined by displacement of toluol in the pycnometer used in the work upon the chloride.

Number of determination.	Weight of CdBr₂ in vacuum. Grams.	Weight of toluol displaced in vacuum. Grams.	Density of CdBr₂. 25°/4°.
10	6.1535	1.0201	5.196
11	6.6920	1.1095	5.196

In both of these analyses the boat was somewhat attacked and a small amount of metallic platinum was found suspended

[1] Proc. Am. Acad., **17**, 29 (1882).
[2] *Ibid.*, **39**, 250 (1903).

in the fused salt. But since the platinum was not removed from the boat during the determination of the specific gravity of the salt, no error could have resulted from this cause. A vacuum correction of $+0.00009$ was applied to every apparent gram of the cadmium bromide.

A discussion of the earlier determinations of the specific gravities of the salts under consideration is impossible, since no descriptions of the experiments are given. In no case is there evidence of any attempt at purification. Slight variations in specific gravity are to be expected as the result of differences in treatment of a salt, but the great disagreement of our results with previous values cannot be explained in this way. Moreover, Bödeker's work on densities has already been shown to be inaccurate in many cases.[1] The great pains which was taken in the purification of our salts and in the carrying out of the determinations leads us to the conclusion that our results represent very nearly the truth. Certainly it is almost inconceivable that they should be too high. Our cadmium chloride, in especial, showed the outward appearance of sufficient purity for even an atomic weight determination. Such an investigation is now in progress.

To sum up the results of this research :

1. Pure anhydrous cadmium chloride was prepared.

2. A pycnometer was devised for the determination of the density of very hygroscopic substances.

3. The specific gravities of the following fused salts at $25°$ referred to water at $4°$ were determined :

Silver bromide	6.478
Cadmium chloride	4.049
Cadmium bromide	5.196

We are indebted to Dr. Wolcott Gibbs and to the Cyrus M. Warren Fund for Research for many indispensable platinum vessels.

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[1] Richards. Proc. Am. Acad., **31**, 163. See also following paper in this JOURNAL.

THE SPECIFIC GRAVITY OF ZINC CHLORIDE.

BY GREGORY PAUL BAXTER AND ARTHUR BECKET LAMB.

Two chief obstacles arise in the determination of the specific gravity of zinc chloride, the extremely hygroscopic character of the substance, and the great tendency which it shows to form a basic salt when heated in a moist condition. Lorentz[1] and Czepinski[2] have found that only by electrolysis of the fused salt could the last traces of water be eliminated. Since the removal of water by electrolysis seemed impracticable for the purpose in hand, recourse was had to the method of heating the double chloride of zinc and ammonium, $ZnCl_23NH_4Cl$,[3] in a current of dry hydrochloric acid gas until all of the ammonium chloride had been expelled. The double salt crystallizes without water of crystallization, and is not hygroscopic, hence it seemed reasonable to suppose that an anhydrous product could be thus obtained. A similar method has been used already by Richards and Parker[4] in preparing dry magnesium chloride, and by Baxter and Hines[5] in the preparation of dry cadmium chloride.

In order to settle this point, a quantity of the double salt was prepared by dissolving the proper amounts of ammonium and zinc chlorides in water, then evaporating the solution nearly to saturation and allowing the solution to cool. The resulting zinc ammonium chloride was highly crystalline, and stable in the air. In order to remove as far as possible the adhering and included water, it was exposed for several days in a finely powdered condition in a desiccator over sulphuric acid and finally over phosphorus pentoxide. Samples of the salt, contained in a porcelain boat, were heated in a hard glass tube in a current of dry hydrochloric acid gas for from one to two hours, at first gently, but finally with the full heat of two Bunsen burners. The residual fused salt, when dissolved in pure water, gave a clear solution, hence it must have been free from oxychloride. Furthermore, this solution

[1] Ztschr. anorg. Chem., 10, 85.
[2] Ibid., 19, 228.
[3] Ztschr. anorg. Chem., 37, 199 (1903).
[4] Proc. Am. Acad., 32, 59.
[5] See preceding paper in this JOURNAL.

gave no test for ammonia with Nessler's reagent. Zinc ammonium chloride is, then, a suitable source of anhydrous zinc chloride ; therefore a quantity of the pure double salt was prepared.

Purification of Materials.

Nine hundred cc. of pure concentrated hydrochloric acid were diluted with twice this volume of water and shaken with a few crystals of potassium permanganate, to set free any bromine or iodine which might have been present. It was then distilled through a platinum condenser and the middle fraction of about 600 cc. was collected in a platinum vessel. In order to prepare ammonia free from amines, ammonium chloride was boiled with concentrated nitric acid and a solution of the recrystallized salt was heated with an excess of sodium hydroxide. A solution of this ammonia was distilled into some of the above hydrochloric acid in a platinum dish, and the resulting ammonium chloride was recrystallized several times from the purest water.

Two hundred and fifty grams of zinc were treated with about 3 liters of 10 per cent sulphuric acid and the containing flask was allowed to stand upon a steam-bath for a week, until nearly all of the zinc had dissolved. Since on cooling the solution some basic salt was precipitated, a few drops of concentrated sulphuric acid were added to dissolve the basic salt, and then hydrogen sulphide was passed into the solution until considerable precipitate had been formed. The precipitate, which consisted chiefly of zinc sulphide, was white from the very first, showing that only traces of metals of the copper group could have been present. The filtered solution was heated for some time with about 10 cc. of concentrated nitric acid, in order to oxidize completely any ferrous salt, and a quantity of very pure sodium hydroxide, sufficient to produce permanent precipitation, was added. After several days' standing, the precipitate of zinc carbonate and ferric hydroxide was removed by filtration and a few cubic centimeters of strong sodium hydroxide solution were added. This solution had been electrolyzed in order to free it from heavy metals until,

when the platinum cathode was treated with hydrochloric acid, no trace of iron could be detected in this acid. As the precipitate produced by the hydroxide gave a test for iron with potassium thiocyanate, treatment with small amounts of sodium hydroxide was repeated three times until iron could be no longer detected in the precipitate, and then was repeated once again. The zinc sulphate in solution was recrystallized four times from a dilute solution of pure sulphuric acid, which had been added to decrease the solubility of the sulphate. A large quantity of sulphuric acid could not be used, since it prevented the formation of the heptahydrate, by diminishing the aqueous tension of the solution. In order to convert the sulphate into the chloride, metallic zinc was next obtained by electrolysis. The zinc sulphate crystals were dissolved in a minimum amount of water, and ammonia was distilled into the solution until it became clear. The solution was then electrolyzed in a shallow glass dish between platinum electrodes, with a current as large as the heating of the solution would permit. The tree of zinc crystals was frequently removed[1] and the crystals were washed with dilute ammonia and water.[2] In the subsequent processes only platinum vessels were used in the purification. About 25 grams of the pure zinc were dissolved in hydrochloric acid which had been purified as already described. Solution took place stormily, because, no doubt, of a small amount of platinum which the zinc contained, the greater part of which remained undissolved. Mylius and Fromm[3] observed the same phenomenon whenever they had electrolyzed zinc solutions between platinum electrodes. Ammonia, purified as already described, was then passed into the solution of zinc chloride until a slight precipitate had been produced, and a small portion of this solution was saturated with pure ammonia and again electrolyzed. The resulting crystals were placed in the main solution and the whole allowed to stand for a month. During this

[1] Reynolds and Ramsay : J. Chem. Soc., Trans., **51**, 854.
[2] The method employed for the purification of the zinc was essentially that used by Richards and Rogers in their investigation upon the atomic weight of zinc. See Proc. Am. Acad., **31**, 160.
[3] Ztschr. anorg. Chem., **9**, 161 (1895).

time any platinum in solution must have been precipitated. To the solution, after filtration, the amount of pure ammonium chloride necessary to form the double salt was added, the solution was then evaporated to saturation, and the crystals of double salt which separated on cooling were twice recrystallized from the purest water. The mother-liquors were evaporated to dryness and used in the preliminary experiments. Finally the purified salt was dri⌒d by prolonged standing over sodium hydroxide in a desiccator, with frequent pulverization.

Method of Experimentation.

The determination of the specific gravity of zinc chloride was carried out in the same manner and with the same apparatus as in the work upon cadmium chloride and bromide by Baxter and Hines.[1] The zinc ammonium chloride, contained in a platinum boat, was first heated in a current of dry hydrochloric acid gas to remove the ammonium chloride. But the boiling-point of this salt lies so near the temperature necessary to drive off the ammonium chloride that in the preliminary experiments either all the ammonium chloride was not removed or else such a small quantity of zinc chloride remained that it was impossible to make an accurate determination of specific gravity. These difficulties were finally avoided by heating gently at first, and almost wholly on top, then raising the temperature as rapidly as the boiling would permit, until no more ammonium chloride was deposited in the cooler parts of the tube. The full heat of two Bunsen burners, one above and one below, was finally applied for about ten minutes. The entire fusion required about an hour and a half. After the tube had been allowed to cool, the hydrochloric acid was displaced by dry nitrogen, and this, in turn, by dry air. The boat was next transferred to a weighing-bottle, without exposure to moist air, by means of the bottling apparatus usually employed for the purpose in this laboratory. The weight of the zinc chloride was then determined.

The pycnometer employed consisted of the weighing-bottle

[1] See preceding paper.

used in the weighing of the salt, into which a pycnometer stopper had been carefully ground. After the weighing of the salt the ordinary stopper was removed and sufficient dry toluol was introduced to cover the salt. The weighing-bottle was then placed in a vacuum-desiccator which was exhausted by means of an air-pump. Finally the pycnometer stopper was inserted and the pycnometer was filled with toluol exactly to a mark on the stem, while the system was immersed in a constant temperature-bath at 25°. The room in which the adjustment was carried out was kept at a temperature within a few tenths of a degree of 25° during the experiment. The thermostat itself was divided into two compartments, so arranged that the pycnometer, immersed as far as possible in water in the inner compartment, was below the level of the water in the outer compartment. After being filled, the pycnometer was wiped with a damp cloth and allowed to stand in the balance case a short time before it was weighed.

After an experiment was completed, the salt, which was translucent, was dissolved in water, a clear solution being always obtained. The aqueous solution was then tested with Nessler's reagent for ammonia, invariably with negative results. A trace of platinum was visible in the fused salt, but was too small in amount to be determined. This platinum may have had its source in the attacking of the boat, although this did not lose in weight perceptibly, or it may have been due to incomplete removal of the platinum introduced during the electrolysis of the zinc. In one case the toluol from the pycnometer was treated with a solution of ammonium sulphide, without the formation of a trace of precipitate, showing that zinc chloride is insoluble in toluol.

The toluol was freed from methylthiophene by repeated shaking with concentrated sulphuric acid, then washed with water, and, after standing over fused sodium hydroxide for some time, was distilled. The end fractions were discarded, although the boiling-point did not perceptibly change during the distillation. The following successive determinations of its specific gravity were carried out with an Ostwald pycnometer :

	Weight of pycnometer. Grams.	Weight of pycnometer filled with water. Grams.	Weight of pycnometer filled with toluol. Grams.
1	7.6536	16.0094	14.8707
2	7.6533	16.0094	14.8707
3	7.6534	16.0095	14.8707
4	7.6533	16.0094	14.8707
5	7.6534	. . . . . .	. . . . . .
Averages,	7.6534	16.0094	14.8707

From these data the density of our toluol at $25°$ referred to water at $4°$ is found to be 0.86138, a value which is identical with that of the sample prepared by Baxter and Hines.

In the following table are given the results of five consecutive determinations of the specific gravity of fused zinc chloride. A vacuum correction of $+0.00027$ was applied to every apparent gram of salt. Since the air displaced by the system filled with toluol with and without the salt was the same, no vacuum correction for the toluol was necessary :

Number of experiment.	Weight of zinc chloride in vacuum. Gram.	Weight of displaced toluol in vacuum. Gram.	Density of zinc chloride. $25°/4°$.
1	0.3036	0.0901	2.902
2	0.5982	0.1792	2.875
3	0.9671	0.2860	2.913
4	0.3232	0.0946	2.943
5	0.9243	0.2742	2.904
		Average,	2.907

The average of Experiments 3 and 5, in which the largest quantities of material were used, is 2.908. If each experiment is weighted according to the quantity of salt employed, the mean value becomes 2.905. Such slight differences are beyond the limit of accuracy of the work, since the maximum amount of toluol displaced was never as much as 0.3 gram. There can be no doubt that the specific gravity of fused zinc chloride is slightly less than 2.91.

The only other determination of the specific gravity of zinc chloride of which we have been able to find mention, was made by Bödeker in 1860,[1] who obtained the value 2.753. In

[1] Die Beziehung zwischen Dichte und Zusammenhang bei festen und liquiden Stoffen.

the light of the difficulty in preparing the salt in a pure condition, it is easy to see why his result is lower than ours, for the presence of water would have had the effect of lowering the observed density.

Needless to say, the weights were carefully standardized to tenths of a milligram, and the corrections for the thermometer at 0° and 32°.38 were determined. Reagents were purified whenever this seemed necessary. Water was distilled twice, once over alkaline potassium permanganate and once over dilute sulphuric acid with a block-tin condenser. In short, every precaution was taken that would be necessary in the most accurate analytical work. The appearance and behavior of the zinc chloride was such as to warrant the assumption of sufficient purity for an atomic weight investigation. Such an investigation is planned for the near future.

We are indebted to Dr. Wolcott Gibbs and to the Cyrus M. Warren Fund for Research for many indispensable platinum vessels.

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THE NEPHELOMETER, AN INSTRUMENT FOR DETECTING AND ESTIMATING OPALESCENT PRECIPITATES.

BY THEODORE WILLIAM RICHARDS AND ROGER CLARK WELLS.

The gravimetric determination of the finely divided scanty precipitate commonly called an opalescence is a very difficult matter, yet this type of quantitative estimation is often required in analytical work, and is very necessary in many investigations of atomic weights. The apparatus here described is designed to determine these precipitates in quantities under 1 or 2 milligrams per liter of suspending solution. Most of the experiments were made with silver chloride, but the apparatus and method are widely applicable. The method depends upon the facts that these precipitates reflect light, and that the intensity of the light reflected is a function of

the quantity of precipitate, when other conditions are constant.

Before giving a description of the present apparatus it might be well to mention the forms used by previous investigators. Gay-Lussac, the inventor of the volumetric method of estimating silver, does not seem to have used any special apparatus for judging the amount of opalescence. Mulder,[1] however, kept his flasks, containing silver chloride, in metallic boxes blackened upon the inside, and usually observed the production of an opalescence in a solution by raising the flask into the diffused light of a room near a window. Sometimes he decanted the mother-liquor into small vials in which he produced and compared opalescent precipitates. His comparison, however, was wholly a matter of judgment; no measuring device entered into it.

Stas[2] constructed an instrument for estimating the amount of suspended precipitate. Four tubes with perfectly plain bottoms, about 4 cc. in diameter, were supported, adjacent to each other, upon a shelf over holes of the same diameter as the tubes. Beneath the shelf was placed an illuminated scale, and everything above the shelf was in darkness. When the marks on the scale, viewed through two heights of opalescent solution, appeared equally illuminated, Stas assumed that there was an equal weight of precipitate in the two volumes. The great disadvantage of this instrument is that the light is transmitted through the precipitate. If, instead, the reflected light is observed, when a powerful beam is allowed to fall upon the precipitate obliquely, the delicacy of the estimation is greatly increased.

Depending upon the latter fact, the instrument which one of us devised several years ago and named the "nephelometer" was better adapted to compare opalescent precipitates. As it has already been described in a paper upon the atomic weight of strontium,[3] it will suffice to mention the essential characteristics. Two test-tubes were arranged almost vertically, but slightly inclined toward one another so that the eye could

1 Mulder : Die Silber Probiermethode, p. 23, Trans., Grimm. Leipzig, 1859.

2 Stas : Œuvres, I, 155 (1894).

3 Richards : Proc. Am. Acad., **30**, 385 (1894).

look into both. Around the test-tube were two opaque sliding jackets. When the slides were adjusted so that the incident light was cut off in such measure as to give equal opalescence in the two tubes, the precipitate was taken as inversely proportional to the lengths exposed to the light. This relation does not hold accurately for dense precipitates, since the nearer portion partly hides the more distant ones ; but for slight opalescence the error is not great, especially when the lengths are not very different. With care, considerable accuracy could be attained, but to secure good results, long practice was necessary.

In order to reduce the uncertainty of comparison due to the inevitable distance between the centers of the two test-tubes, this instrument has been modified and improved. In its present form the instrument is shown in the figure on the following page. There are three separate parts, the main frame A, which holds the tubes in position, a movable top B, containing adjustable prisms, and a large box C, in which is a source of light.

The tubes destined to hold the solutions under examination were test-tubes of clear glass free from striations, and containing each 0.032 liter, painted outside around the top and bottom with black asphalt paint. These opaque bands form the most convenient method of obliterating reflections from the meniscus and the curved bottom of the test-tube. The space between the lower edge of the upper band and the bottom of the tube was exactly the same in each case. The lower edge of the upper band projected below the wooden support, P, in order to provide a sharp line of demarcation between light and darkness, as well as to allow the tubes to be shut into complete darkness by the sliding jackets, S, S. The tubes rested upon equal wooden pillars (which guided the sliding jackets) and projected well above the support, P, in order to preserve their cleanliness. The sliding jackets were also of glass, thickly painted. They moved up and down over the test-tubes, shutting off as much light as was wished and being held in any desired place by a brass spring. When raised, they disclosed below two scales which indicated exactly the lengths of the tubes above exposed to the light.

Front   Side
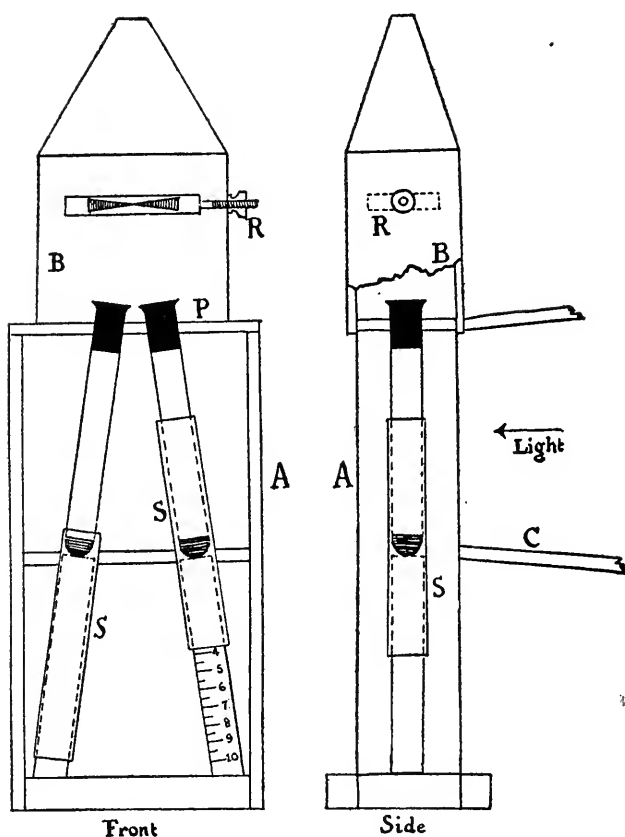
Upon the frame rested the small box B, which shut out all light, and yet was easily removable. In this box was a small frame which could be adjusted to any position by means of the set screw R. This frame contained two 15° prisms with their thin edges together, the edges having been ground slightly by an optician until they fitted closely. The effect of the prisms when looking downwards through them is to bring into view, side by side, semicircular images of about half of each tube, so that the two halves appear scarcely larger than a single tube, the dividing line being barely visible. The appearance of the image resembles the field of a half-shadow

polarimeter. The success of the instrument lies in this arrangement of the prisms. Different observers can judge the equality of two tubes to within a few per cent, an accuracy impossible with the older nephelometer where the mind had to estimate the small differences at a distance ; under favorable conditions successive readings of the scale by one observer will not vary so much as a millimeter.

For stirrers, propeller-shaped pieces of platinum foil were sealed upon two glass rods. These stirrers seemed to insure a more efficient mixing with less danger of contamination than the process of decanting back and forth between two tubes, as recommended by Stas. They were always kept standing in separate tubes of pure water when not in use.

The apparatus was thoroughly tested by comparing with its aid solutions containing known amounts of freshly precipitated argentic chloride in suspension. Its efficiency is most easily seen in a series of results where portions of the same opalescent liquid were placed in the two tubes for comparison. This procedure obviates any possible inconsistency arising from unequal speed of precipitation—a matter to be discussed in a subsequent paper.

In the manipulation the most scrupulous care must be taken to avoid the introduction of dust, which usually contains chloride enough to affect the test. Hydrochloric acid gas is also an insiduous source of contamination. The tubes were filled until the meniscus rose above the upper blackened rim, and were then placed in a light-shield,—a large box blackened inside. The outer surfaces of the tubes were always wiped with a very clean cotton cloth, and the incandescent electric light used as a source of illumination was only turned on during the few minutes required for the readings. During this short time no sensible darkening of the precipitate occurs, since the light is deficient in violet and ultraviolet rays.

Below are given the results obtained with three pairs of tubes, each containing an opalescent liquid with 2 milligrams of argentic chloride suspended in a liter of solution. The suspension of this small amount of substance had been effected

by adding a considerable excess of argentic nitrate to a suitable solution of chloride, which is thus practically all precipitated.

Comparison of Similar Solutions.

Heights of equal intensity.

	Tube *a.*	Tube *b.*	Ratio $\frac{a}{b}$.
	mm.	mm.	
Pair 1	53	52	1.02
	53	55	0.96
	53	53.5	0.99
		Average,	0.992
Pair 2	53	51	1.04
	53	54	0.98
	53	55	0.96
		Average,	0.997
Pair 3	53	56	0.95
	53	51	1.04
	53	54	0.98
	77	77	1.00
	34.2	34.2	1.00
	67	64	1.05
		Average,	100.3

Total average, 0.998 ± 0.001

The close agreement of these readings shows the absence of any constant error greater than 1 per cent either in the prisms, the tubes, the lighting, or the scale. Evidently, too, the length of the tube exposed to the light makes no difference ; but, nevertheless, in practice, settings were usually made at several different heights. The actual error (0.2 per cent) of the mean of the twelve settings corresponds to only 0.00005 milligram of argentic chloride, and the maximum deviation (5 per cent) of a single observation from the true value corresponds to 0.0015 milligram. Thus the instrument is capable of a considerable degree of accuracy.

To determine the soluble chloride in an unknown solution— for example, the filtrate from a large mass of precipitated argentic chloride—suitable volumes of a known standard solution and of the unknown solution, were made up to equal volumes in the respective tubes. A milliliter of the standard

solution of sodic chloride used for this particular comparison was equivalent to 0.00526 milligram of silver chloride. To preserve it from contamination it was kept in a large bottle with a burette attached, out of all contact with the outside air, save through a tube containing cotton wool. The unknown solution was always introduced into the right-hand tube of a pair by means of a pipette, to the left-hand tube was added the desired volume of standard solution, and then pure water was added to each. After stirring, a milliliter of a solution of silver nitrate, equivalent to 1 milligram of silver, was added to both tubes. Stirring shortens the time required for precipitation, but care must be used that no minute spatterings spring from one tube to the other. Even then, long time is required to attain complete precipitation, two hours at least being needed for comparative accuracy, and as much as fifteen hours for the greatest precision of which the method is capable. The presence of an electrolyte, such as nitric acid or sodic nitrate, greatly accelerates the passage from the colloidal to the solid condition, and lessens the time required. Since this question concerns rather the mechanism of a particular reaction than the working of the apparatus, the detailed discussion of our results in this direction will be reserved for a future paper.

Since a small trace of accidentally admitted chloride so profoundly vitiates the result the greatest care is necessary in every step of the operation. Even the distilled water of the laboratory sometimes showed traces of chloride, if it had stood long in unstoppered flasks. All the substances used in these experiments (except the standard solution of salt) were completely free from traces of chloride, and all apparatus connected with the work was kept unusually clean with large quantities of redistilled water. The purest water was redistilled into a large bottle, through a special adapter for excluding dust. When the adapter was removed, a tube containing soda replaced it so that no trace of hydrochloric acid from the air could enter the bottle when water was withdrawn through a siphon. It is to be noted that hydrochloric acid almost always exists in the atmosphere of a laboratory in which bottles of the solution are kept.

Below are given three typical experiments determining the quantity of silver chloride found in a certain solution according to the method described above.

		Standard solution. Milliliters.	Unknown solution. Milliliters.	Ratio of the scale readings.	Silver chloride per liter found. Milligram.
Exp.	1	5.00	10.00	0.85	2.24
"	2	4.40	10.00	1.01	2.29
"	3	4.30	10.00	0.99	2.24
					2.26

These results illustrate sufficiently the degree of accuracy which may be easily obtained, as well as the best method of proceeding. The first comparison is made with solutions only approximately equal, and the succeeding observations are made upon tubes containing quantities of substance, computed from the first trial, which are much more nearly equal. In this way the greatest accuracy may be reached.

The instrument may be used similarly in many other cases when a finely divided precipitate reflects light, and provides an unusually sensitive means of detecting very faint cloudiness in a liquid. Care must be taken to have both standard solution and unknown solution subjected to precisely the same conditions, for varying conditions of precipitation may lead to differences in the appearance of the precipitate far greater than the possible optical error of the apparatus. Herein lies the chief caution to be noted in its use. By modifying the apparatus in such a way as to provide a bright background, the arrangement might be a very convenient device for the colorimetric comparison of transparent liquids.

The contents of this paper may be summarized as follows : An instrument for the comparison of opalescent mixtures is described, the essential advantage of which lies in the optical juxtaposition of the fields of view to be compared, by means of prisms. This improvement over the earlier nephelometer increases the ease and accuracy of the setting. The instrument, thus improved, is able to detect and estimate very small amounts of suspended precipitate. The chief possi-

bility of error lies in the state of the precipitated material. In order to exclude variation here, the solution to be estimated and the standard solution for comparison should be precipitated in exactly the same way.

THE ADDITION OF ACID SULPHITES TO CINNAMYLIDENEMALONIC ACID.

By Elmer P. Kohler.

Cinnamylidenemalonic acid contains the combination of single and double linkages which Thiele has called a "conjugated system of vicinal double unions."[1] According to Thiele such a system should be represented by the general formula

$$>C=CH.CH=C<,$$

in which the dotted lines denote "partial valences." When a substance that has this kind of a chain combines with a molecule of another substance the combination is supposed to take place through the partial valences, and the successive steps in the process of addition are supposed to be represented by the following formulas:

$$>C=CH.CH=C< \;\longmapsto\; >CA-CH.CH-CA< \;\longmapsto$$
$$A \qquad\qquad A$$
$$>CA-CH=CH-CA<.$$
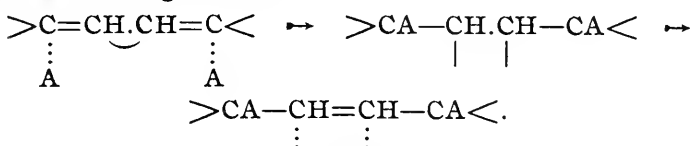
This view can be tested by determining the structure of the product. If addition takes place as here represented, then the product must have the addends in combination with the carbon atoms at the extremities of the conjugated system, and a new "active" double linkage in the middle. Thiele and others have shown that this is undoubtedly true in a number of cases in which the addends are of the same kind, as, for example, two hydrogen atoms or two bromine atoms.

It is not so well established that combination may take place in this way when the addends are not of the same kind.

[1] Ann. Chem. (Liebig), 306, 94.

Meisenheimer[1] and Thiele[2] have recently found a plausible explanation for the peculiar behavior of some nitro compounds by assuming that an alcoholate can combine at the ends of a conjugated system as follows:

$$>C=CH.N=O + ROK = >CR-CH=N-OK.$$
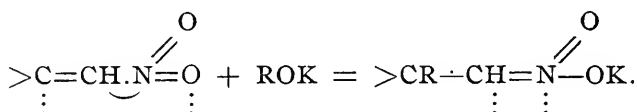
It is difficult, however, to establish the structure of metallic derivatives like these, and no case is known where dissimilar addends combine at the ends of a conjugated system composed entirely of carbon atoms.

While studying the action of light on cinnamylidenemalonic acid,[3] I found that the substance combines with acid sulphites in the cold. Since the aliphatic sulphonic acids are stable, well-defined substances there seemed to be an opportunity, here, for studying the addition of dissimilar groups to conjugated systems. One case of direct addition to the acid has already been described. Thiele and Meisenheimer[4] found that when the methyl ester of the acid combines with 1 molecule of hydrocyanic acid, the cyanogen group goes into the β-position instead of into the Δ-position as they had anticipated. This addition, therefore, involves only the double union nearest the carboxyl groups.

It has also been shown[5] that in direct sunlight the acid rapidly goes into a tetramethylene derivative:

$$2C_6H_5CH : CH.CH : C\begin{cases}CO_2H\\CO_2H\end{cases} =$$

$$C_6H_5CH-CHCH : C\begin{cases}CO_2H\\CO_2H\end{cases}$$
$$HO_2C\begin{cases}\\\end{cases}C : HC-CH-CHC_6H_5$$
$$HO_2C$$
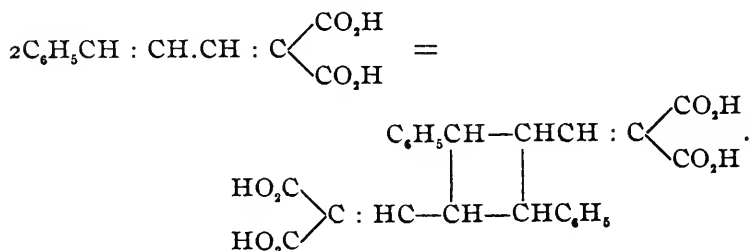
[1] Ann. Chem. (Liebig), **323**, 205.
[2] *Ibid.*, **325**, 1.
[3] This JOURNAL, **28**, 239.
[4] Ann. Chem. (Liebig), **306**, 247.
[5] Ber. d. chem. Ges., **35**, 2411.

This change, which is essentially one of addition, involves only the double union nearest the phenyl group.

The results described below show that when the acid combines with 1 molecule of an acid sulphite, the sulphoxyl group goes into the β-position. The structure of the resulting product was established by the following reactions.

When a solution of the neutral potassium salt that is obtained as the direct product of addition is acidified, an unstable acid salt is precipitated :

$$C_6H_5CH : CHCHCH\underset{\underset{SO_3K}{|}}{<}\overset{CO_2K}{\underset{CO_2K}{}} + 2HCl =$$

$$C_6H_5CH : CHCHCH\underset{\underset{SO_3K}{|}}{<}\overset{CO_2H}{\underset{CO_2H}{}} + 2KCl.$$
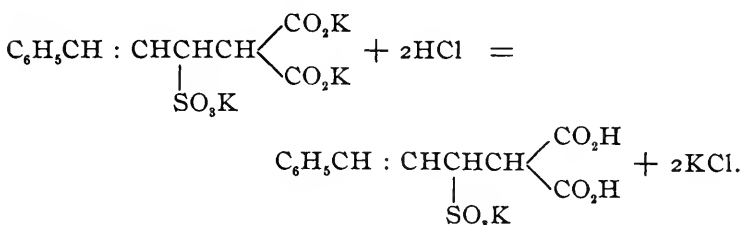
This, on heating, loses carbon dioxide :

$$C_6H_5CH : CHCHCH\underset{\underset{SO_3K}{|}}{<}\overset{CO_2H}{\underset{CO_2H}{}} = C_6H_5CH : CHCHCH_2CO_2H.$$
$$\underset{SO_3K}{|}$$
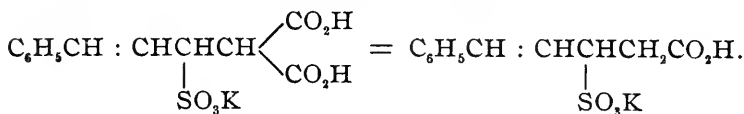
The resulting acid salt is oxidized to benzaldehyde, carbon dioxide, and β-sulphopropionic acid :

$$C_6H_5CH : CHCHCH_2CO_2H + 3O =$$
$$\underset{SO_3H}{|}$$

$$C_6H_5CHO + \left[\underset{\underset{SO_3H}{|}}{CO_2HCHCH_2CO_2H} \right] \mapsto \underset{\underset{CH_2SO_3H}{|}}{CH_2CO_2H} + CO_2.$$
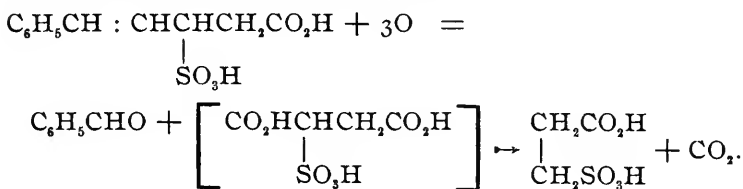
When an aqueous solution containing molecular quantities of acid potassium sulphite and cinnamylidenemalonic acid is allowed to stand in the cold the sulphite slowly diminishes in quantity, and at the end of four or five days the solution no longer gives a reaction for sulphites. The liquid then contains two salts—the potassium salt of benzalsulphoethylmalonic acid,

$$C_6H_5CH : CH.CHCH \underset{SO_3K}{\overset{}{|}} \diagdown_{CO_2K}^{CO_2K},$$

and the potassium salt of benzalsulphobutyric acid,

$$C_6H_5CH : CH.CHCH_2CO_2K. \\ | \\ SO_3K$$
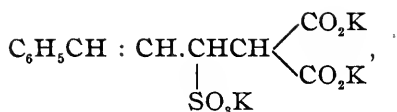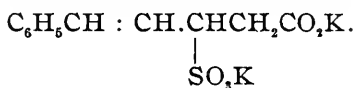
By warming a similar solution on the water-bath the same change may be completed in half an hour.

The same two salts are obtained when potassium sulphite is added to a solution of the acid potassium salt of cinnamylidenemalonic acid, and when sulphur dioxide is slowly passed into a solution containing potassium sulphite and the neutral salt of the unsaturated acid. These salts crystallize only from very concentrated solutions, and it was not possible to separate them from each other by systematic fractional crystallization of the mixture. It was found, however, that the salt of benzalsulphoethylmalonic acid is less soluble in a strong solution of potassium hydroxide than the salt of benzalsulphobutyric acid, and a method of separation was based on this difference.

The Potassium Salt of Benzalsulphoethylmalonic Acid.

To prepare this salt the calculated quantity of acid potassium sulphite was added, gradually, to a hot solution obtained by neutralizing the unsaturated acid with potassium carbonate. The liquid was warmed on a water-bath until it no longer gave a yellow precipitate of unchanged unsaturated acid when acidified with dilute acids. It was then cooled in ice-water and poured into a cold solution (1 : 4) of potassium hydroxide. The shining white plates that separated were filtered off immediately, washed with a more dilute solution of potassium hydroxide, and recrystallized from water. An analysis gave the following results :

    I. 0.3241 gram salt lost 0.0259 gram at 130°.

   II. 0.2628 gram salt lost 0.0213 gram at 130°.

  III. 0.2415 gram salt gave 0.1390 gram K_2SO_4.

IV. 0.2215 gram salt gave 0.1294 gram K_2SO_4.

	Calculated for $C_{12}H_9O_7SK_3.2H_2O$.	I.	II.	III.	IV.
			Found.		
H_2O	7.97	8.00	8.12	....	....
K	26.06	....	....	25.80	26.18

The salt is very easily decomposed. If the aqueous solution is boiled for a few hours and acidified, the yellow, unsaturated acid is precipitated, showing that the reaction

$$C_6H_5CH : CH.CH : C\begin{matrix} CO_2H \\ CO_2H \end{matrix} + KHSO_3 =$$

$$C_6H_5CH : CHCHCH\begin{matrix} CO_2H \\ | \\ SO_3K \end{matrix} \begin{matrix} CO_2H \\ CO_2H \end{matrix}$$
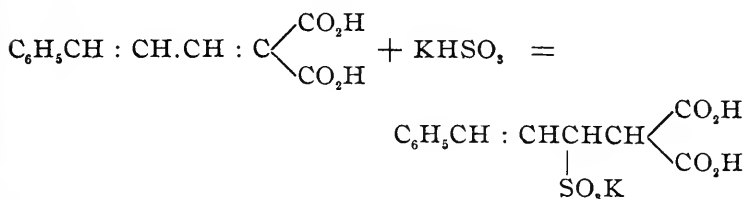
is reversible. Solutions of alkalies split off acid sulphite in the cold. The salt is also decomposed by acids, the result depending upon the concentration of the acid. When cold, concentrated hydrochloric acid is added to a saturated solution of the salt, the solution immediately becomes yellow, and in a short time the unsaturated acid begins to separate. When dilute hydrochloric acid is added to a solution of the salt, colorless acid salts are precipitated in well-formed crystals. These acid salts are stable when dry, but they cannot be recrystallized, as they steadily lose carbon dioxide even when dissolved in cold water. Analyses of various precipitates indicated mixtures of mono- and dipotassium salts.

The Acid Potassium Salt of Benzalsulphobutyric Acid.

This salt is obtained in calculated quantity when dilute hydrochloric acid is added to a boiling solution of the neutral salt described above. It is, however, much easier to make the salt directly from cinnamylidenemalonic acid. Potassium sulphite is added, in small quantities, to the finely powdered acid suspended in boiling water. Each addition of the sulphite causes a rapid evolution of carbon dioxide. The sulphite is added until a test with dilute hydrochloric acid shows the absence of unsaturated acid. The liquid then contains the potassium salt of benzalsulphobutyric acid along with

some of the potassium salt of benzalsulphoethylmalonic acid. To remove the latter, a considerable quantity of dilute hydrochloric acid is added and the liquid warmed until a test with hot concentrated hydrochloric acid shows the absence of the salt. The sparingly soluble acid potassium salt of benzalsulphobutyric acid crystallizes from this solution on cooling. The salt is obtained in calculated quantity. It is easily purified by recrystallization from water. A potassium determination gave the following results :

I. 0.1494 gram salt gave 0.0441 gram K_2SO_4.
II. 0.2393 gram salt gave 0.0696 gram K_2SO_4.

	Calculated for $C_{11}H_{11}O_6SK$.	I.	Found. II.
K	13.30	13.23	13.10

The salt crystallizes in plates that are readily soluble in boiling water, sparingly soluble in cold water, insoluble in alcohol. It is much less easily decomposed than the potassium salt of benzalsulphoethylmalonic acid. No change could be detected when a solution in water or in dilute hydrochloric acid was boiled for eight hours. When a solution of 10 grams of the acid in concentrated hydrochloric acid was boiled for eight hours, and subsequently extracted with ether, the latter took up a small quantity of a substance which, after recrystallization from alcohol, melted at 165°. This was cinnamenylacetic acid. A similar change takes place when the salt is heated with alkalies. Five grams of the substance were dissolved in cold potassium hydroxide and the solution set aside. No sulphite could be detected in the solution after it had stood for several days. On warming the solution on a water-bath a new salt began to separate in thin, colorless plates. This was the potassium salt of cinnamenylacetic acid. The solution contained potassium sulphite.

The *neutral potassium salt* of benzalsulphobutyric acid, obtained by neutralizing the acid potassium salt with potassium carbonate, is very soluble in water. As it was not obtained in well-defined crystals it was not analyzed.

The *calcium salt* is easily obtained by neutralizing the acid potassium salt with calcium carbonate or, better, by adding a

solution of calcium chloride to a solution of the neutral potassium salt and evaporating to crystallization. It is moderately soluble in cold water, somewhat more readily in boiling water. It crystallizes in needles containing 3 molecules of water of crystallization.

I. 0.5100 gram substance lost 0.0791 gram H_2O at 140°.

II. 0.1732 gram substance gave 0.0673 gram $CaSO_4$.

	Calculated for $C_{11}H_{10}O_5SCa.3H_2O$.	Found. I.	II.
H_2O	15.54	15.50	....
Ca	11.51	....	11.43

The *barium salt* was obtained by adding a solution of barium chloride to a solution of the potassium salt. It is moderately soluble in boiling water and crystallizes from hot, saturated solutions in needles. It is partly decomposed by prolonged boiling with water.

I. 0.1548 gram salt gave 0.0922 gram $BaSO_4$.

II. 0.2122 gram salt gave 0.1258 gram $BaSO_4$.

	Calculated for $C_{11}H_{10}O_5SBa$.	Found. I.	II.
Ba	35.09	34.98	34.89

Benzalsulphobutyric acid was made from the barium salt. The barium was precipitated with a slight excess of dilute sulphuric acid, the excess of the latter removed by boiling with lead carbonate, and the lead that went into solution precipitated as sulphide. On evaporating the solution obtained in this way, the acid separated as a compact mass of colorless needles. After one recrystallization from water the acid melted sharply at 76°. An analysis gave the following results :

I. 0.2141 gram substance gave 0.4035 gram CO_2 and 0.0925 gram H_2O.

II. 0.1860 gram substance gave 0.3499 gram CO_2 and 0.0893 gram H_2O.

	Calculated for $C_{11}H_{12}O_5S$.	Found. I.	II.
C	51.53	51.46	51.31
H	4.72	4.84	4.80

The acid is not hygroscopic. It is readily soluble in water,

alcohol, and acetone; almost insoluble in ether and chloroform. It can be recrystallized from ether containing water. When heated in a capillary tube it begins to decompose, visibly, at 125° to 130°. In open vessels it slowly decomposes at the temperature of boiling water. Sulphur dioxide is given off. The residue solidifies, on cooling, to a resinous mass that is only partly soluble in a solution of sodium carbonate. From this solution acids precipitate the cinnamenylacetic acid which melts at 165°. None of the allo-acid, melting at 136°, appears to be formed.

Oxidation of Benzalsulphobutyric Acid.

The acid and its salts instantly reduce neutral, alkaline, and acid solutions of permanganates. In neutral and alkaline solutions it was impossible to get an oxidation-product that contained more than a trace of a sulphonic acid—the sulphoxyl group is split off as sulphate even when the oxidation is carried out at 0° in very dilute solution.

A solution of barium permanganate was added, drop by drop, to a solution that was kept at 0° with cracked ice. When the color of the permanganate appeared in the liquid the solution was decolorized with a small quantity of the potassium salt and filtered. The filtrate was acidified with sulphuric acid and extracted with ether. The ether, on evaporation, left only benzoic acid. The extracted liquid was digested with lead carbonate to remove the excess of sulphuric acid. A small quantity of lead that went into solution was precipitated with hydrogen sulphide and the filtrate from the lead sulphide evaporated to dryness. The potassium salts that separated contained only a trace of sulphur. Since they did not crystallize well they were turned into calcium salts by boiling with a strong solution of calcium chloride. The sparingly soluble calcium salt that separated was dissolved in hot, dilute hydrochloric acid. This solution, on cooling, deposited the characteristic crystals of acid calcium malate.

The main products obtained by oxidizing benzalsulphobutyric acid in neutral or alkaline solutions are sulphuric acid, benzoic acid, and malic acid. Since these products

show nothing with reference to the structure of the acid, it was necessary to undertake the oxidation in acid solution.

Preliminary experiments showed that in the presence of acids very little sulphuric acid is formed, even if the substance is oxidized in a boiling solution. The oxidation was, therefore, carried out as follows : A solution containing 10 grams of the potassium salt and 15 grams of phosphoric acid was heated to boiling in a flask closed with a rubber stopper with 3 holes. A glass tube connected with a steam generator passed through one of the holes, a dropping-funnel through another, and a delivery-tube, connected with a condenser, through the third. The condenser was closed by a receiver that was connected with a wash-bottle containing a solution of barium hydroxide. A solution of barium permanganate was added, drop by drop, to the liquid, which was kept boiling by a rapid current of steam. In a short time benzaldehyde began to collect in the receiver, and at the same time barium carbonate was precipitated in the wash-bottle. The addition of permanganate was continued until the purple color no longer disappeared immediately. The precipitated phosphates and oxides were then filtered off and the filtrate extracted with ether. The ether, on evaporation, left a small quantity of benzoic acid. The extracted liquid was heated to boiling and treated with a solution of barium hydroxide until the reaction was alkaline. This precipitated all of the manganese and phosphoric acid, but left a little barium in solution. After removing this in the usual way, the liquid was evaporated to small volume and allowed to cool. A very soluble potassium salt crystallized out in small, colorless crystals. After one recrystallization from water this gave the following analytical results :

I. 0.1852 gram substance lost 0.0136 gram at 135°.
II. 0.3148 gram substance lost 0.0229 gram at 135°.
III. 0.2115 gram substance gave 0.1485 gram K_2SO_4.
IV. 0.1820 gram substance gave 0.1281 gram K_2SO_4.

	Calculated for $C_8H_4SO_5K_2.H_2O$.	I.	II.	III.	IV.
			Found.		
H_2O	7.25	7.32	7.28	....	....
K	31.52	....	....	31.50	31.61

The salt has the composition of a potassium salt of sulpho-propionic acid. When a solution of the salt was boiled with a strong solution of barium chloride the characteristic barium salt of β-sulphopropionic acid separated out.

The products obtained by oxidizing benzalsulphobutyric acid are benzaldehyde, benzoic acid, carbon dioxide, and β-sulphopropionic acid. The sulphoxyl group must, there-fore, be in the β-position with reference to the carboxyl group and only one double linkage is involved when acid sulphites combine with cinnamylidenemalonic acid.

The Action of Bromine on Benzalsulphobutyric Acid.

When a drop of bromine is added to a moderately concen-trated, cold, aqueous solution of the acid a blood-red, amor-phous precipitate separates while the liquid remains colorless. In contact with the liquid, the precipitate immediately begins to lose its color. The liquid first becomes milky, then clears up again and a colorless substance crystallizes out in very small, lustrous crystals. If these crystals are allowed to re-main in contact with the liquid they slowly disappear, and in the course of a few hours the liquid becomes as clear as it was at the beginning. This process may be repeated until the solution contains 2 atoms of bromine for every molecule of unsaturated acid. After that the bromine remains un-changed.

Similar changes take place when bromine is added to aqueous solutions of the salts of the acid. In solutions of the acid potassium, acid sodium, and acid ammonium salts bro-mine produces a red precipitate provided the concentration exceeds 1 part of salt in about 100 parts of the solution. If the concentration is less than this and greater than 1 part of salt in about 1500 parts of water, the colorless substance crys-tallizes out without the intermediate precipitation of the red substance. In still more dilute solutions the bromine is de-colorized without the formation of a precipitate.

In aqueous solutions of the neutral potassium, calcium, and barium salts, bromine also produces a red precipitate, provided the solutions contain at least 1 part of salt in 250 parts of

water. In more dilute solutions the bromine is rapidly decolorized, but no precipitate forms. When the resulting solutions are acidified the same colorless substance obtained in the preceding cases crystallizes out.

The red precipitate obtained in all these cases seems to be a peculiar addition-product of 2 atoms of bromine to a molecule of benzalsulphobutyric acid or a molecule of one of its salts. I have not as yet succeeded in getting a pure substance from any of the solutions. The precipitate formed from the acid is so unstable that most of it becomes colorless before it can be removed from the liquid. It does not form in the absence of water and does not exist in solution. The precipitates formed from salts are more stable than that formed from the acid. A rough comparison gave the following results : The precipitate formed from a solution of 0.02 gram-molecule of the acid in 20 cc. of water completely lost its color in twenty minutes, that from 0.02 gram-molecule of the acid potassium salt in two weeks, and that from 0.02 gram-molecule of the neutral potassium salt in about three months. When these precipitates are rapidly dried in a vacuum or on drying plates they apparently retain their color indefinitely, but no two preparations give the same analytical results. In appearance and general properties the substances resemble the oxonium compounds of unsaturated ketones, etc. For the present their structure remains unknown.

The colorless substance obtained by adding bromine to dilute solutions of benzalsulphobutyric acid was dried on filter-paper and recrystallized from ether. A qualitative analysis showed the presence of sulphur and bromine, and combustions gave the following results :

I. 0.2424 gram substance gave 0.3494 gram CO_2 and 0.0693 gram H_2O.

II. 0.2919 gram substance gave 0.4220 gram CO_2 and 0.0840 gram H_2O.

	Calculated for $C_{11}H_{11}BrO_5S$.	Found. I.	Found. II.
C	39.30	39.39	39.44
H	3.28	3.18	3.19

The substance has the composition of an acid that would be derived from benzalsulphobutyric acid by addition of 1 molecule of bromine and subsequent loss of 1 molecule of hydrobromic acid.

$$C_6H_5CH : CHCHCH_2CO_2H \longrightarrow C_6H_5CHCHCHCH_2CO_2H \longrightarrow$$
$$\qquad\qquad | \qquad\qquad\qquad\qquad\quad |\ \ |\ \ |$$
$$\qquad\qquad SO_3H \qquad\qquad\qquad\qquad Br\ Br\ SO_3H$$

$$C_6H_5CH : CBrCHCH_2CO_2H$$
$$\qquad\qquad\quad |$$
$$\qquad\qquad\quad SO_3H$$
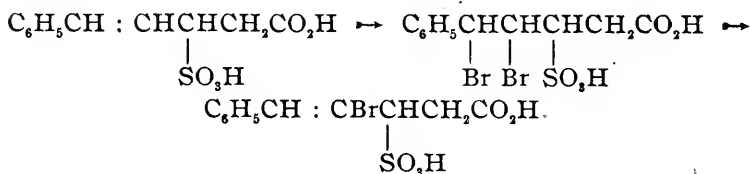
It appeared highly improbable, however, that a sulphonic acid of this structure would not be more soluble than 1 part in 1500 parts of water. It seemed much more likely that the substance is a sultonic acid analogous to the lactonic acids that are formed by the action of bromine on β,γ-unsaturated dibasic acids. The basicity determinations pointed in the same direction, since they showed that the substance is a monobasic acid that becomes dibasic when warmed with alkalies. The results are as follows :

In the cold, 0.1645 gram substance neutralized 0.0194 gram sodium hydroxide instead of 0.0192 gram calculated for a monobasic acid ; and 0.1742 gram substance neutralized 0.0199 gram sodium hydroxide instead of 0.0208 gram calculated. When warmed with an excess of sodium hydroxide 0.1825 gram substance neutralized 0.0415 gram sodium hydroxide instead of 0.430 gram calculated for a dibasic acid.

When the substance is dissolved in boiling water and then neutralized, the amount of base required lies between the amounts calculated for a monobasic and a dibasic acid. A monobasic acid, with the composition of the substance under consideration, may be either a sultonic acid or a lactonic acid, as shown by the following formulas, which represent two out of a number of possibilities :

$$\qquad\qquad\qquad\qquad\qquad\qquad O\text{------}CO$$
$$\qquad\qquad\qquad\qquad\qquad\qquad |\qquad\ |$$
$$C_6H_5CHCHBrCHCH_2CO_2H \qquad C_6H_5CHBrCHCHCH_2$$
$$\quad\ \ |\qquad\qquad\ \ | \qquad\qquad\qquad\qquad\qquad\ |$$
$$\quad\ \ O\text{-------}SO_2 \qquad\qquad\qquad\qquad\qquad\ SO_3H$$
$$\qquad\qquad I. \qquad\qquad\qquad\qquad\qquad\qquad II.$$
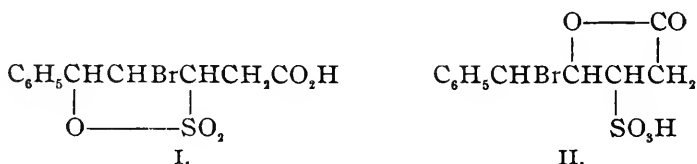
It is easy to decide between two formulas like these, since a substance with the structure represented by I. should form stable esters, while the esters of sulphonic acids can be obtained only through the sulphone chlorides and are easily hydrolyzed.

The esters of the acid in question are obtained with the greatest ease and they can be hydrolyzed only by prolonged boiling with dilute acids.

The *methyl ester* was prepared by dissolving the acid in absolute methyl alcohol to which a few drops of sulphuric acid had been added, and warming the solution for a short time on the water-bath. The ester separated in crystalline form on cooling. It was recrystallized from methyl alcohol and analyzed :.

0.2670 gram substance gave 0.4025 gram CO_2 and 0.0870 gram H_2O.

	Calculated for $C_{12}H_{13}BrO_5S.$	Found.
C	41.26	41.11
H	3.75	3.62

The ester melts at 148°. It is readily soluble in chloroform, ether, and in boiling alcohol; moderately soluble in cold alcohol and in ligroin ; insoluble in water. It crystallizes in large, colorless prisms.

The *ethyl ester* very closely resembles the methyl ester. It melts at 121°.

0.2166 gram substance gave 0.3398 gram CO_2 and 0.0806 gram H_2O.

	Calculated for $C_{13}H_{15}BrO_5S.$	Found.
C	42.97	42.76
H	4.13	4.13

These results suffice to show that the substance is a sultonic acid, but they do not prove that the sultone ring is closed in the γ-position as represented ; nor do they show the location of the halogen atom. The substance has been transformed in a variety of different ways but the results cannot

be interpreted definitely until these points are established. They will, therefore, be reserved for a later paper.

CHEMICAL LABORATORY,
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November, 1903.

THE ADDITION OF IODINE AND POTASSIUM IODIDE TO ORGANIC COMPOUNDS CONTAINING THE CARBONYL GROUP.

BY A. M. CLOVER.

When iodine, potassium iodide, and benzophenone are brought together in solution, and the solvent removed by evaporation, the residue contains a crystalline substance of a golden luster. When the three substances are melted together and the product allowed to cool, a crystalline residue of the same appearance is obtained.

The compound just mentioned may be obtained in a pure state by recrystallizing the crude product from ether or chloroform. If an excess of iodine has been used, this must be removed by pulverizing the crude product and allowing it to remain in a vacuum : otherwise the iodine is dissolved by the solvent and crystallizes out with the compound. It is more convenient, however, to use an excess of the other constituents, as these are completely separated from the compound on recrystallizing.

The compound was found to consist of iodine, potassium iodide, and benzophenone, each of which may be recovered unchanged. The crystals are very soluble in acetic ether, acetic acid, and acetone ; moderately soluble in chloroform, ether, and alcohol, and sparingly soluble in benzene, carbon disulphide, and ligroin. In dilute solution the substance is dissociated into its constituents. When the crystals are shaken with benzene, the iodine and benzophenone gradually go into solution and the potassium iodide is deposited as a residue. The crystals melt at about 100°, and above this point the vapor of iodine may be detected. When shaken with water they are slowly dissociated, the iodine and potassium iodide going into solution and the benzophenone being

left as a residue. This change is hastened by the addition of an immiscible solvent such as chloroform.

It was found that the crystals obtained have the same composition, regardless of the proportion in which the constituents are brought together. If an excess of benzophenone was used, this remained in the mother-liquor on recrystallizing. An excess of potassium iodide remained as a residue on dissolving the crude product. An excess of iodine was removed in a vacuum or by dissolving the compound in a small amount of acetic ether, filtering from excess of iodine and potassium iodide, and then removing the solvent by evaporation in a vacuum.

The substance was finally prepared by mixing 8 parts of benzophenone with 4 parts of iodine and 3 parts of potassium iodide. The mixture was warmed to 100° and the melted product stirred for several minutes. It was then poured into a dish and allowed to cool. The solid product was then pulverized and recrystallized from ether or chloroform by dissolving at ordinary temperature and cooling in a freezing-mixture. The crystals obtained were filtered without suction and then packed together tightly on a porous plate in order to remove all mother-liquor. The crystals obtained from chloroform were found to have a slightly different composition from those out of ether. This difference is due to the fact that in each case the solvent enters into the compound. In each case the crystals are hexagonal prisms whose sides have a golden luster and whose bases are dark-blue. Those from chloroform are much larger and better defined.

Methods of Analysis.

(1) The iodine was estimated by covering the substance with a solution of potassium iodide, adding a few drops of chloroform, and shaking until the compound was completely dissociated. The solution was then titrated with a standard solution of sodium thiosulphate.

(2) The potassium iodide was estimated by determining the total iodine in the compound and subtracting from this

the free iodine obtained in (1). The total iodine was estimated by covering the substance with 10 cc. of a saturated aqueous solution of sulphur dioxide, in a small flask, warming slightly, and shaking until the color of iodine had entirely disappeared. The contents of the flask were then cooled and the benzophenone pulverized with a glass rod. The solution was then carefully filtered and the iodine determined by means of standard solutions of silver nitrate and ammonium thiocyanate.

(3) The benzophenone was determined by direct weighing after the removal of the other constituents. The substance was placed in a small flask and covered with about 10 cc. of benzene. Molecular silver was then added and the contents of the flask warmed gently and shaken until the iodine had been completely removed. The benzophenone dissolved in the benzene was then carefully and completely removed from the flask and filtered into a dish from which the solvent was then removed by evaporation in a vacuum. Preliminary experiments with known quantities of benzophenone showed that it could be accurately estimated in the presence of the other two substances by this method.

Substance Crystallized from Chloroform.—After drying on a porous plate, the crystals are contaminated with a small amount of uncombined iodine. This may be completely removed by allowing them to remain in a vacuum for two hours with frequent agitation. After this time the substance continues to lose weight at a uniform rate in a vacuum and much slower at ordinary pressure. For analysis, the substance was allowed to remain in a vacuum for two hours. The loss in weight of the pure substance, in this time, is inconsiderable.

Sample 1 :

0.2714 gram substance required 12.67 cc. N/20 thiosulphate.

0.2715 gram substance required 16.25 cc. N/20 silver nitrate.

Sample 2 :

0.2501 gram substance required 11.7 cc. N/20 thiosulphate.

0.3387 gram substance required 20.32 cc. N/20 silver nitrate.

Sample 3 :

0.2933 gram substance required 13.58 cc. N/20 thiosulphate.

0.2303 gram substance required 10.69 cc. N/20 thiosulphate.

0.2004 gram substance required 11.92 cc. N/20 silver nitrate.

0.2844 gram substance gave 0.1562 gram benzophenone.

0.3051 gram substance gave 0.1687 gram benzophenone.

Sample 4, crystallized twice :

0.3291 gram substance required 15.4 cc. N/20 thiosulphate.

Determination of the total halogen in the compound, by the method of Carius, gave results much higher than those obtained above. From these results it was concluded that the substance contains chloroform of crystallization.

Sample.	Free iodine. Per cent.	Total iodine. Per cent.	Benzophenone. Per cent.
1	29.58	37.93	....
2	29.67	38.05	...
3	{ 29.32 { 29.46	37.70	{ 54.92 { 55.29
4	29.68	....	....
Average,	29.58	37.89	55.10

Potassium iodide, by difference, 10.88 per cent.

Total iodine, potassium iodide, and benzophenone, 95.56 per cent.

Combining ratio between iodine and potassium iodide, $\frac{7.11}{2}$.

Combining ratio between benzophenone and potassium iodide, $\frac{9.22}{2}$.

The three constituents are therefore combined in the ratio of 9 : 7 : 2. The substance contains 1 molecule of chloroform and is represented by the formula $(C_{13}H_{10}O)_9(KI)_2I_7, CHCl_3$.

	Calculated.	Found (by difference).
Chloroform	4.01	4.44

Substance Crystallized from Ether.—The crystals obtained from ether contain only a trace of uncombined iodine, for samples analyzed immediately after drying did not show a

much higher percentage of iodine than those which had remained in a vacuum for an hour or more. The substance loses in weight slowly on standing in a desiccator at ordinary pressure and more rapidly in a vacuum. One gram substance lost 3 milligrams in weight on standing for three days in a desiccator at ordinary pressure. The loss in weight is probably due to loss of ether of crystallization rather than iodine, for an analysis of this sample made at the end of ten days showed no loss in the percentage of iodine.

Sample 1, crystallized twice :

0.2831 gram substance required 13.55 cc. N/20 thiosulphate.

Sample 2 :

0.2562 gram substance required 12.36 cc. N/20 thiosulphate.

0.2961 gram substance required 18.24 cc. N/20 silver nitrate.

0.2470 gram substance required 15.32 cc. N/20 silver nitrate.

Sample 3 :

0.2325 gram substance required 11.28 cc. N/20 thiosulphate.

0.2980 gram substance gave 0.1662 gram benzophenone.

0.2914 gram substance gave 0.1626 gram benzophenone.

Sample.	Free iodine. Per cent.	Total iodine. Per cent.	Benzophenone. Per cent.
1	30.34	....	....
2	30.60	$\begin{cases} 39.07 \\ 39.33 \end{cases}$	....
3	30.77	....	$\begin{cases} 55.77 \\ 55.79 \end{cases}$
Average,	30.57	39.20	55.78

Potassium iodide, by difference, 11.29 per cent.

Total iodine, potassium iodide, and benzophenone, 97.64 per cent.

Combining ratio between iodine and potassium iodide, $\dfrac{7.08}{2}$.

Combining ratio between benzophenone and potassium iodide, $\dfrac{8.9}{2}$.

The compound evidently contains ether of crystallization and is represented by the formula $(C_{13}H_{10}O)_9(KI)_2I_7,C_4H_{10}O$.

	Calculated.	Found (by difference).
Ether	2.52	2.36

It will be noted that, disregarding the solvent, the formulas of the crystals obtained from the two solvents are the same.

Benzoic Anhydride Compound.

Benzoic anhydride forms a compound very similar to the one just described. It has a high luster, the shade of which lies between a golden and a steel-gray. The crystals are deposited from solution in the form of a stringy mesh, from which it is very difficult to remove the solvent. The substance is much more stable than the benzophenone compound. As in the previous case, it was found that regardless of the proportion in which the constituents were brought together, the purified product had always the same composition. The crude product was most easily prepared by melting together 13 parts of benzoic anhydride with 6 parts of iodine and 3 parts of potassium iodide. It may also be obtained by adding a strong solution of iodine in potassium iodide to a solution of the anhydride in acetic acid, the compound being precipitated.

An excess of either of the constituents in the crude product was removed in the manner already described under the benzophenone compound. The substance has about the same solubilities as the benzophenone compound except that it is only sparingly soluble in ether and chloroform. It is also dissociated in very dilute solution. It is best purified by recrystallizing in a freezing-mixture from absolute alcohol or from a mixture of equal volumes of acetic ether[1] and chloroform. The crystals are less difficult to filter if the solution be agitated during the crystallization.

For analysis, the substance was filtered with suction and pressed out on a porous plate, finally to a powder. It then remained in a vacuum for four or five hours, having been frequently repulverized. It was found that the substance obtained from either solvent continued to lose in weight slowly in a vacuum and more slowly in a desiccator at ordinary pressure.

Three grams substance from absolute alcohol lost 1 milligram after being twelve hours in a vacuum.

[1] The acetic ether used here and in other parts of this work was anhydrous and free from alcohol.

Two and five-tenths grams substance from acetic ether-chloroform lost 0.7 milligram after eighteen hours in a desiccator at ordinary pressure.

The substance melts at 125° to 128°; there is no noticeable dissociation of iodine below this point.

Samples of the substance purified by both methods were analyzed. The estimation of the constituents was made in the same way as with the previous compound, except that in the estimation of anhydride a small amount of acetic ether was used with the benzene as the compound is almost insoluble in pure benzene. Careful tests showed that benzoic anhydride could be accurately estimated in the presence of iodine and potassium iodide by this method.

Sample 1, crystallized from acetic ether and chloroform :
0.2982 gram substance required 13.8 cc. N/20 thiosulphate.
0.3320 gram substance required 15.35 cc. N/20 thiosulphate.
0.3321 gram substance required 20.9 cc. N/20 silver nitrate.
0.2601 gram substance required 16.35 cc. N/20 silver nitrate.
0.2943 gram substance gave 0.1669 gram benzoic anhydride.
0.2779 gram substance gave 0.1576 gram benzoic anhydride.

Sample 2, crystallized from absolute alcohol :
0.3042 gram substance required 14.16 cc. N/20 thiosulphate.
0.2791 gram substance required 17.6 cc. N/20 silver nitrate.
0.2633 gram substance required 16.7 cc. N/20 silver nitrate.
0.3415 gram substance gave 0.1928 gram benzoic anhydride.
0.4105 gram substance gave 0.2324 gram benzoic anhydride.

Sample 3, crystallized from absolute alcohol :
0.3243 gram substance required 14.9 cc. N/20 thiosulphate.
0.2070 gram substance required 12.93 cc. N/20 silver nitrate.
Sample 4, crystallized from acetic ether and chloroform.
0.3109 gram substance required 14.34 cc. N/20 thiosulphate.

Sample.	Free iodine. Per cent.	Total iodine. Per cent.	Benzoic anhydride. Per cent.
1	$\begin{cases} 29.35 \\ 29.30 \end{cases}$	$\begin{cases} 39.92 \\ 39.84 \end{cases}$	$\begin{cases} 56.71 \\ 56.71 \end{cases}$
2	29.52	$\begin{cases} 39.96 \\ 40.22 \end{cases}$	$\begin{cases} 56.45 \\ 56.61 \end{cases}$
3	29.14	39.58	....
4	29.25	....	....
Average,	29.31	39.85	56.62

Potassium iodide, by difference, 13.79 per cent.

Total iodine, potassium iodide, and benzoic anhydride, 99.72 per cent.

Combining ratio between iodine and potassium iodide, $\frac{2.78}{1}$.

Combining ratio between benzoic anhydride and potassium iodide, $\frac{3.01}{1}$.

If the substance has the composition $(C_{14}H_{10}O_3)_3, KI, I_3$, the product obtained is not pure. As the analysis of different samples gave practically the same figures and as the total of constituents, found, amounts to almost 100 per cent, it is quite probable that the product is pure and accordingly the simplest formula to be assigned is $(C_{14}H_{10}O_3)_{12}, (KI)_4, I_{11}$.

A determination of the molecular weight by the cryoscopic method was deemed useless on account of the known tendency of these substances to dissociate in solution.

Phthalic Anhydride Compound.

For the preparation of this compound an excess of phthalic anhydride was melted with iodine and potassium iodide. The product solidified, on cooling, to a highly lustrous, green, crystalline mass, which was pulverized. The compound was dissolved away from the excess of anhydride by means of a small amount of acetic ether. The filtered solution was then treated with 3 volumes of chloroform and the compound obtained by crystallizing in a freezing-mixture.

When excess of iodine was used in the preparation it was removed in a vacuum, and the compound purified in the same way had the same composition as in the previous case.

The crystals were filtered without suction and then packed tightly on a porous plate to remove all mother-liquor. They then remained in a vacuum for four or five hours before analysis. When kept in a vacuum for some time, the crystals on top lose their luster, showing dissociation, but the loss in weight is inconsiderable.

Two grams lost 0.6 milligram, in a vacuum for three hours.

The same sample lost 0.4 milligram after standing sixteen hours in a desiccator at ordinary pressure.

The substance is only sparingly soluble in chloroform and ether. It is moderately soluble in alcohol, but is dissociated, anhydride separating out.

When added to water it soon dissociates, all of the products going into solution.

The crystals are fine and irregular in shape. They are dark-green in color and have a beautiful luster.

Sample 1 :

0.2854 gram substance required 23.44 cc. N/20 thiosulphate.

Sample 2 :

0.2447 gram substance required 20.1 cc. N/20 thiosulphate.

0.2038 gram substance gave 0.1479 gram CO_2 and 0.0165 gram H_2O.

Sample 3 :

0.3291 gram substance gave 0.3964 gram AgI (substance dissolved in water and iodine reduced with sulphur dioxide).

0.2698 gram substance required 22.1 cc. N/20 thiosulphate.

Sample 4 :

0.1970 gram substance required 16.09 cc. N/20 thiosulphate.

0.2408 gram substance required 24.7 cc. N/20 silver nitrate.

0.2159 gram substance gave 0.1550 gram CO_2 and 0.0166 gram H_2O.

Sample.	Free iodine. Per cent.	Total iodine. Per cent.	Anhydride. Per cent.
1	52.09	....	....
2	52.11	....	30.60
3	51.95	65.08	....
4	51.77	65.05	30.25
Average,	51.98	65.06	30.42

Potassium iodide, by difference, 17.12 per cent.

Total iodine, potassium iodide, and phthalic anhydride, 99.52 per cent.

Combining ratio between iodine and anhydride, $\frac{1.99}{1}$.

Combining ratio between iodine and potassium iodide, $\frac{3.97}{1}$.

The compound is therefore represented by the formula $(C_8H_4O_3)_2, KI, I_4$.

Phenylacetic Anhydride Compound.

Two grams anhydride were mixed with 2 grams iodine and 1 gram pulverized potassium iodide. The mixture was heated to 50° and stirred for several minutes. At a higher temperature the iodine seemed to act destructively upon the anhydride. The crude product was then cooled and triturated with a small amount of chloroform to dissolve out any unchanged anhydride or its decomposition-product. After filtering, the residue was placed in a vacuum for the removal of uncombined iodine. The substance was then recrystallized from chloroform and dried on a porous plate. The substance loses weight, on standing, much more rapidly than the compounds previously described. The analyses were therefore made soon after the substance had been prepared and allowed to remain in a vacuum for a few minutes.

One and one-tenth grams substance remained in vacuum for three-fourths of an hour and was found to have lost 8 milligrams.

The same sample then lost 16 milligrams, after seven hours, in a desiccator at ordinary pressure.

The loss in weight is continuous and is due to combined iodine, as the substance has the odor of iodine and free iodine was noted in the containing vessel after standing for some time.

The substance is very soluble in ether, alcohol, acetic ether, and acetone ; moderately soluble in chloroform ; insoluble in benzene.

The analyses were made in the same way as those of the

benzophenone and benzoic anhydride compounds. In the estimation of total iodine concordant results could not be obtained. The per cent of potassium iodide was, therefore, found by difference, assuming that the substance contains no solvent.

Sample 1 :

0.2331 gram substance required 18.97 cc. N/20 thiosulphate.

0.2652 gram substance required 21.48 cc. N/20 thiosulphate.

Sample 2 :

0.1459 gram substance required 11.9 cc. N/20 thiosulphate.

0.1678 gram substance required 13.7 cc. N/20 thiosulphate.

0.2727 gram substance gave 0.0961 gram phenylacetic anhydride.

0.4281 gram substance gave 0.1479 gram phenylacetic anhydride.

Sample 3 :

0.1724 gram substance required 14.15 cc. N/20 thiosulphate.

0.2502 gram substance gave 0.0875 gram phenylacetic anhydride.

0.2110 gram substance gave 0.0748 gram phenylacetic anhydride.

Sample.	Free iodine. Per cent.	Anhydride. Per cent.
1	$\begin{cases} 51.62 \\ 51.37 \end{cases}$	· · · · · · · ·
2	$\begin{cases} 51.73 \\ 51.78 \end{cases}$	$\begin{cases} 35.24 \\ 34.55 \end{cases}$
3	52.09	$\begin{cases} 34.97 \\ 35.40 \end{cases}$
Average,	51.77	34.78

Potassium iodide, by difference, 13.45 per cent.

Combining ratio between iodine and anhydride, $\frac{2.98}{1}$.

Combining ratio between iodine and potassium iodide, $\frac{5.04}{1}$.

The simplest formula to be assigned to this substance is, therefore, $(C_{16}H_{14}O_3)_5,(KI)_3,I_{15}$.

Succinic Anhydride Compound.

This compound is less stable and more difficult to purify

than the ones previously described. When the constituents are melted together the residue solidifies, on cooling, to a golden crystalline mass.

It is in most cases impossible to obtain the crystals pure by recrystallization on account of the dissociation of the substance in dilute solution, and because of the slight solubility of the dissociated succinic anhydride in all of the organic solvents. Various solvents were tried, but only from a mixture of acetic ether and chloroform could the substance be obtained in a fair degree of purity.

Six grams succinic anhydride were melted with 4 grams iodine and 2.5 grams pulverized potassium iodide. The residue was cooled and pulverized and dissolved in about 10 cc. acetic ether and the solution filtered. Fifteen cc. chloroform were then added and the solution was again filtered. On cooling in a freezing-mixture, about 1 gram of the compound separated out. It was dried on a porous plate and kept in a vacuum ten minutes before analysis. The substance is apparently free from uncombined iodine. It loses iodine rapidly in a vacuum, but only very slowly at ordinary pressure.

0.2296 gram substance required 17.53 cc. N/20 silver nitrate.
0.2169 gram substance required 11.1 cc. N/20 thiosulphate.
Another sample was prepared in the same manner.
0.1151 gram substance required 5.45 cc. N/20 thiosulphate.
The substance is probably represented by the formula $(C_4H_4O_3)_4, KI, I_2$.

	Calculated.	Found. I.	II.
Free iodine	30.9	32.46	30.03
Total iodine	46.4	48.42	....

Other crystalline anhydrides and ketones were found to form compounds similar to those described, as shown by the luster of the product obtained.

The power to form these compounds evidently depends upon the carbonyl group, which is common to anhydrides and ketones. Other substances containing this group were found to form such compounds, while with ethers, alcohols, and phenols they could not be obtained.

When benzanilide (excess) is melted with iodine and potassium iodide, the cooled product possesses a golden luster. With nitrobenzoyl chloride the same luster may be obtained, but it is less decided and may be due to the presence of nitrobenzoic anhydride as an impurity. Methyl oxalate (excess) gives a light-green luster on cooling the product. The luster disappears on warming and the compound is evidently very unstable.

Iodine and potassium iodide are together dissolved by acetone in large amounts, although singly these substances have only a small solubility in the solvent. Acetic anhydride behaves similarly to acetone. It may be concluded that compounds are formed with each of these substances, although it is impossible to isolate the compounds in these cases. With ether, however, the solubility of iodine and potassium iodide is not noticeably increased when both are present and there is no evidence of the formation of a compound. When the phenyl ether of trimethyleneglycol (the substance was selected because of its being a solid) is brought together with iodine and potassium iodide, there is no evidence of the formation of a compound.

The compounds selected for study in this work are representative ones. It was thought that possibly these compounds would be found to be of simple and uniform composition. Careful analysis, however, has shown that the composition is variable and, in most cases, complex.

LABORATORY OF GENERAL CHEMIS-
TRY, UNIVERSITY OF MICHIGAN,
ANN ARBOR, Nov. 20, 1903.

THE ACTION OF AMMONIA UPON COPPER SULPHATE SOLUTIONS.

BY JAMES LOCKE AND JACOB FORSSALL.

INTRODUCTION.

The various investigations which have recently been published on the nature of the compounds formed by treatment of a copper sulphate solution with ammonia[1] go to show that a

[1] Reychler: Bull. soc. chim., (III.), **13**, 387 (1895); Konowaloff: J. Russ. Phys. Chem. Soc., **31**, 910 (1899); Dowson and McCrae: J. Chem. Soc. (London), **77**, 1239 (1900); Gaus: Ztschr. anorg. Chem., **25**, 236.

complex radical results which contains not more than 4 mole-
cules of ammonia to 1 atom of copper. Konowaloff, on deter-
mining the vapor-tension of the ammonia in such solutions
by a dynamical method, found that for each molecule of cupric
sulphate from 3.4 to 4.04 molecules of ammonia were ab-
sorbed, according to the concentrations employed. His meas-
urements were made at 60°, on very dilute cupric solutions
and with a large excess of ammonia. Reychler ascertained
that the addition of 4 molecules of ammonia to 1 of cupric
sulphate caused only a slight lowering of the freezing-point
of the solution.

Gaus, like Konowaloff, investigated the lowering of the
vapor-pressure of an ammoniacal solution produced by the ad-
dition of cupric sulphate. He used a very delicate dynamical
method. In his investigation, however, he included the be-
havior of salts of a large number of metals in ammonia, but
gives only a few determinations for each. In his two experi-
ments with cupric sulphate and normal ammonia he found the
following :

Gram-molecules Cu^{II} per liter.	Lowering of vapor-pressure. mm
0.0491	2.49
0.0982	5.02

Assuming that ammonia solutions follow Henry's law, and
adopting Gaus' value for the vapor-pressure of normal am-
monia, 13.45 mm., the ratio of found ammonia to copper is
given by the equation

$$\frac{l}{13.45 \cdot Cu} = x,$$

where l is the lowering of the vapor-pressure and x the num-
ber of molecules in the complex. The above two determina-
tions give, respectively, 3.77 NH_3 and 3.80 NH_3, an almost
perfect agreement, although the Cu concentrations are widely
different. From these two experiments Gaus drew the con-
clusion that the lowering of the vapor-tension of the ammo-
nia is directly proportional to the amount of cupric sulphate
added. These results have been to a certain extent confirmed

by us. The ratios of copper to total ammonia in Gaus' experiments, it may be remarked, were 1 : 20.4 and 1 : 10.2, respectively.

The investigation at hand containing the greatest number of experiments is that of Dawson and McCrae. These authors determined the distribution ratio of ammoniacal solutions containing varying quantities of both copper and ammonia, between water and chloroform, and then from the distribution constant of ammonia in aqueous solution alone, between the same media, calculated the amount of ammonia which had passed into combination in each case. They state, themselves, that the results are not very accurate, but deduce from them a mean curve, which gives the following results :[1]

Table I.

Molecules Cu^{II}.	Cu : total NH_3.	Cu : burned NH_3.
0.05	1 : 5	1 : 3.14
0.05	1 : 6	1 : 3.24
0.05	1 : 7	1 : 3.43
0.05	1 : 8	1 : 3.52
0.05	1 : 9	1 : 3.63
0.05	1 : 10	1 : 3.76
0.025	1 : 6	1 : 3.16
0.025	1 : 10	1 : 3.68
0.025	1 : 16	1 : 3.96

If, as is ordinarily assumed, but one complex, $Cu(NH_3)_4$, is formed in these solutions, the gradual change in the ratio of copper to combined ammonia here seen must be due to a change in the condition of equilibrium represented by the equation

$$Cu(NH_3)_4 = k.Cu.[NH_3]^4. \qquad (1)$$
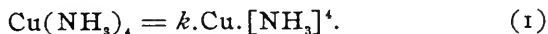
With so wide a variation in the amount of combined ammonia, we should be able to calculate the value of the dissociation constant, k. The concentration of the complex,

$$Cu(NH_3)_4,$$

is given by

$$Cu(NH_3)_4 = \frac{NH_{3_0}-NH_{3_1}}{4},$$

[1] J. Chem. Soc. (London), **77**, 1252.

where NH_{3_0} represents the total ammonia and NH_{3_1} that which has remained uncombined.

Assuming that the small quantity of residual cupric sulphate is fully dissociated, furthermore, the concentration Cu becomes

$$Cu = Cu_0 - \frac{NH_{3_0} - NH_{3_1}}{4},$$

Cu_0 being the total concentration of the copper. Substituting these values in (1), we obtain for k the expression :

$$k = \frac{NH_{3_0} - NH_{3_1}}{[4Cu_0 - (NH_{3_0} - NH_{3_1})]NH_{3_1}^4}.$$

This equation is not at all satisfied by the data of Dawson and McCrae's experiments. They give for k, values which lie anywhere between 47,000 and 1,650. According to the results of these authors (and the same applies to Konowaloff's experiments) the assumption that only one complex exists is very improbable. This becomes evident when we calculate the amount of unaltered copper sulphate presumably left in the solution. In the first experiment cited in Table I., for instance, the concentration of the residual sulphate would be :

$$0.05 - \frac{3.14 \times 0.05}{4} = 0.0105 \text{ gram-molecule per liter.}$$

We must conceive of this amount of copper, outside the complex and not precipitated by a soluble hydroxide, an assumption which is certainly very improbable.

If one complex only is formed, therefore, it must be assumed that the methods thus far employed do not give the correct value for the concentration of the residual ammonia. Either this is the case or we have to do with two complexes,

$$Cu(NH_3)_x \qquad \text{and} \qquad Cu(NH_3)_y,$$
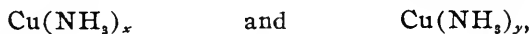
in equilibrium according to the equation

$$Cu(NH_3)_x = k.Cu(NH_3)_y.NH_3^{x-y}.$$
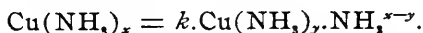
In this case we obtain for k, by a process of reasoning similar to the above, the expression

$$k = \frac{x\mathrm{NH_{3_0}} - \mathrm{NH_{3_1}} - y\mathrm{Cu_0}}{[x\mathrm{Cu_0} - (\mathrm{NH_{3_0}} - \mathrm{NH_{3_1}})]\,\mathrm{NH_{3_1}}^{x-y}}.$$

In this, since x and y are whole numbers, they may be found empirically from two determinations. The formula gives no satisfactory results when tested by Dawson and Mc-Crea's data. It seemed very possible, however, that the equation would be satisfied if only measurements of greater accuracy were available, for since the calculation involves the use of differences, any errors of experiment would be much magnified in the result. The present investigation was undertaken with this object.

The method chosen was the very ingenious process devised by Gaus. It consisted in leading a known volume of electrolytic gas through the solution and then into standardized hydrochloric acid. From the fall in the conductivity of the latter, as it became partially neutralized, the amount of ammonia taken up by the gas was given, and from these data its partial pressure into the solution was calculated. The details of the method as used by us, as well as the form of the apparatus, differed somewhat from those described by Gaus, and may perhaps be advantageously described in full as a criterion of the reliability of our results. Primarily, however, the question as to how far outside influences, in addition to experimental error, interfere with the value of the data, requires discussion.

The four chief factors which may influence the degree to which the vapor-pressure of the ammonia in an ammoniacal cupric sulphate solution is lowered, are :

1. The formation of one or more complex radicals.

2. Decreased or increased solubility of ammonia in a solution of the complex, as compared with its solubility in water.

3. Double decomposition of the sulphate of the complex and ammonium hydroxide, yielding ammonium sulphate. Under this head, also, may be placed the possible formation of basic salts when the concentration of the ammonia is low.

4. Ionization of the complex radical.

Since the problem is to find only the exact amount of am-

monia which has gone to form the complex or complexes, the experimental results are entirely worthless unless we can either neglect the last three of these factors, or apply corrections for them in calculating the amount of the residual ammonia in the solutions.

The question of double decomposition (3) can probably be disregarded. There is no doubt but that the complex base, say $Cu(NH_3)_4.(OH)_2$, is very highly dissociated, and that the distribution of the acid radical between it and ammonium hydroxide would be such as to yield only a very small quantity of ammonium sulphate. Dawson and McCrea found, furthermore, that in a solution of cupric hydroxide in ammonia only 2 molecules of ammonia are absorbed for each one of the cupric compounds. This indicates that if the body $Cu(NH_3)_4(OH)_2$ were formed to any extent by the reaction,

$$Cu(NH_3)_4SO_4 + 2[NH_3 + H_2O] =$$
$$Cu(NH_3)_4(OH)_2 + (NH_4)_2SO_4 ;$$

the secondary process

$$Cu(NH_3)_4(OH)_2 = Cu(NH_3)_2(OH)_2 + 2NH_3$$
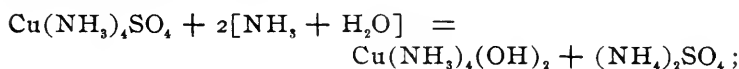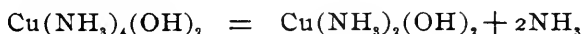
would at once take place, and the same quantity of ammonia would thus be liberated as had been withdrawn through the double decomposition. The total amount of ammonia absorbed would thus remain constant, and in case only one complex were formed, the results would not be vitiated. If two complexes result, the calculation of the amount of each would probably be subject to a slight correction, but we have found that this is not the case. The above argument, of course, does not apply to the possible formation of basic salts when the ratio of ammonia to copper is very low. We have found that in this case the experimental results are unreliable, and they have accordingly been rejected.

The fourth factor, ionization of the complex salt, can, we think, also be disregarded. It would be noticeable only if there were a marked difference in the readiness with which the undissociated complex salt and the complex ion undergo molecular dissociation with loss of ammonia. This, however,

seems not to be the case, for Dawson and McCrae found that the addition of sodium sulphate to their solutions, which should hinder ionization, produced no change in the ratio of copper to combined ammonia.

There remains, therefore, but one disturbing factor, the possible change in solubility of ammonia in water when cupric sulphate is added to its solution. If this decreases its solubility, a given quantity of ammonia would, of course, have a higher vapor-tension in the copper solution than in water, and the ratio of combined ammonia to copper, when determined without applying any correction for this fact, would be less than the actual. This physical effect of the dissolved salt may, indeed, be relatively very great in ammoniacal solutions. Gaus found, in the case of potassium chloride, that in a 0.4 normal solution of this salt the vapor-pressure of normal ammonia was 1 mm. higher than in water alone. This corresponds to the pressure of an 0.075 normal solution of ammonia. The decrease in solubility is, therefore, about 0.19 molecule ammonia for 1 molecule of the potassium salt.

In our own experiments we believe that we have been able to estimate fairly accurately the degree to which this decrease in the solubility interferes with the experimental results, and have found that after introducing the necessary correction, the ratio of copper to combined ammonia becomes 1 : 4 in all the more dilute solutions. In other words, only the one complex, $(Cu(NH_3)_4$, results, and this is formed by virtually all the copper in the solution. An excess of ammonia is required to prevent the decomposition of this radical with precipitation of cupric hydroxide or a basic salt, but owing to the uncertain composition of the latter, the dissociation constant could not be ascertained. That all the copper in the solution passes into the complex would be expected from the behavior of such solutions toward the ordinary analytical reagents for copper, though not at all from the molecular ratios of combined ammonia to the salt, as found by either Gaus or Dawson and McCrae.

Method of Experiment.

Fig. I. shows the form of the apparatus used by us. The

Fig. I.
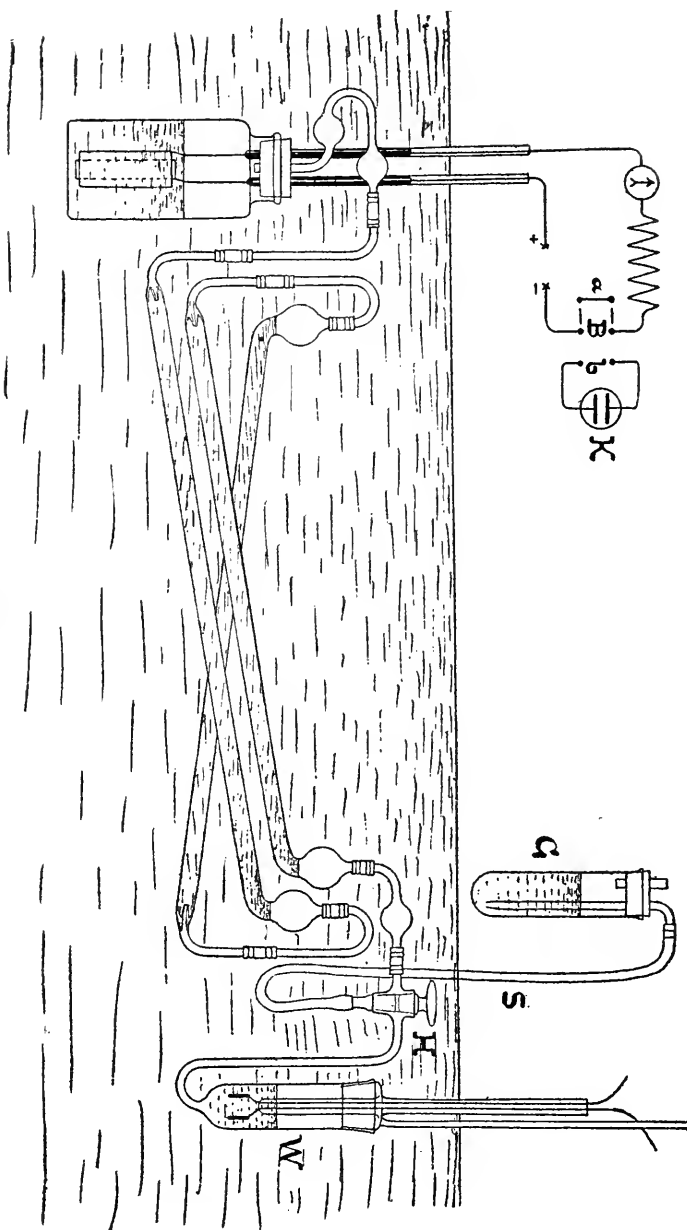
absorption vessels, through which the electrolytic gas passes
on its way to the resistance cell W, were obliquely held glass
tubes of about 50 cc. capacity each.   This seemed prefera-
ble to the arrangement of Gaus, in which they consisted of
spirals of small diameter, within cylindrical bottles, the fear
being that the bubbles of gas, in passing through the spirals,
would be less apt to go through the ammoniacal solution than
to push it before them, thus coming into actual contact with
only a small quantity of the liquid.   All connections were
made with thick-walled rubber tubing, which was tightly
ligatured with wire.   Between the voltmeter and the first
absorption tube, and the last absorption-tube and resistance
cell, were placed bulbs containing cotton, to prevent the re-
spective solutions from being mechanically carried over.
The resistance cell W was not surrounded by paraffin, but,
as Goldschmidt[1] suggests, allowed to stand in direct contact
with the water of the thermostat.   It was fitted with a deep,
ground-glass stopper, the joint with which was sealed by a
mixture of beeswax and rosin.   This stopper carried two
long tubes, one of which was for the exit of the gases, the
other containing the wires leading to the electrodes and sup-
porting the latter.   Contact between the wires was prevented
by running one of them through a thin glass jacket.   To
avoid changes in the capacity of the cell through alterations
in the relative position of the electrodes, with respect to the
vessel itself, small marks were made upon the stopper and the
rim of the cell, and these were always brought opposite each
other.   The amount of acid introduced into the cell was for
the same reason very carefully measured, and always the
same.

The current passed through the voltmeter registered at 0.5
to 1 ampere.   The generation of the electrolytic gas was be-
gun half an hour before the experiment proper, the two-way
cock H during this time being so turned that the gas would
pass through the tube S into G, and thence into the air.
This length of time, in which to establish complete equilib-
rium throughout the apparatus, was found necessary for ob-

[1] Ztschr. anorg. Chem., **25**, 236.

taining coincident results, although Gaus states that two minutes or so are sufficient. The tube G contained water and was employed in order to bring the gases, at the beginning of the experiment, under the same pressure as that to which they are afterward subjected. For this purpose the water column in G was of the same height as that of the hydrochloric acid in the resistance cell. Were it not for this arrangement, a certain amount of time would be required in which to overcome the pressure in the cell, and this would involve a loss.

As soon as equilibrium was secured, the experiment itself was begun. The copper cathode was immersed in the copper voltmeter K and, simultaneously, by the connection with the latter at *b* established, and the cock H so turned that the gases would pass through the capillary tube to the resistance cell. The current was allowed to flow until the resistance in W had increased to a degree indicating the neutralization of about 75 per cent of the acid by ammonia, this requiring from half an hour to an hour and a half. The experiment was then interrupted by taking out the copper cathode and turning off the cock H.

The water in the thermostat was heated by electricity. The temperature, which was regulated by an apparatus devised by Prof. W. R. Whitney, of this Institute, remained constant at 25°, the variations not being more than ±0°.02.

Calculation of the Partial Pressure of the Ammonia.—The total pressure of the mixture of gases entering the resistance cell is made up of the partial pressures.

p_1, of electrolytic gas ;

p_2, of ammonia ;

p_3, of aqueous vapor.

This total pressure is the same as that of the atmosphere (B_0) plus the pressure of the column of liquid in the resistance cell ($= \dfrac{h}{s}$, when h is the height of the liquid and s is specific gravity of Hg).

$$B_0 + \frac{h}{s} = p_1 + p_2 + p_3,$$

whence
$$p_1 + p_2 = B_0 + \frac{h}{s} - p_3,$$

and
$$p_2 = \frac{B_0 + \dfrac{h}{s} - p_3}{\dfrac{p_1}{p_2} + 1}. \tag{I.}$$

Now the partial pressures of the electrolytic gas and ammonia are directly proportional to their volumes, and according to the number of gram-molecules of each (m_1 and m_2) in the mixture. For our purpose the mixture of hydrogen and oxygen may be regarded as a simple gas. We have, therefore,

$$\frac{p_1}{p_2} = \frac{m_1}{m_2}. \tag{II.}$$

m_1, the number of gram-molecules of electrolytic gas, and m_2, that of the ammonia, are given us by the experimental data, as follows :

Notation : Cu = weight of copper precipitated in the copper voltmeter.

m = normality of the acid in the resistance cell.

V = volume of this acid, in cubic centimeters.

P = amount of the acid neutralized by the acid, in percentage.

Since 63.6 grams of precipitated copper are equivalent to 1 gram-molecule of hydrogen and 0.5 gram-molecule of oxygen,

$$M_1 = 1.5 \frac{Cu}{63.6}.$$

The number of gram-molecules of absorbed ammonia is :

$$M_2 = \frac{P}{100} \times m \times \frac{V}{1000} = \frac{mPV}{100,000},$$

and therefore,

$$\frac{M_1}{M_2} = \frac{150,000}{63.6} \frac{Cu}{mPV} = \frac{2358.5\ Cu}{mPV}.$$

Hence, by (I.) and (II.), the expression for p_2 becomes

$$p_2 = \frac{B_0 + \dfrac{h}{s} - p_3}{\dfrac{2358.5 \text{ Cu}}{m\text{PV}} + 1}.$$

p_3, the pressure of the water vapor, is not the same as that over pure water at the corresponding temperature. This is slightly lessened through the dissolved substance. The relative lowering $\dfrac{p-p_3}{p}$, where $p = $ the vapor-pressure over pure water, can be approximately estimated by means of van 't Hoff's formula. The correction for the copper complex formed can be neglected. With normal ammonia it amounts to about 0.42 per cent only. For the ammonia, however, it is more significant. The formula reads

$$\frac{p-p_3}{p} = \frac{1}{N},$$

in which N is the number of molecules of solvent compared with 1 molecule of the solute. If the solution is n-normal, therefore,

$$n = \frac{1000}{18.02.n} \qquad \text{and} \qquad p_3 = p - \frac{18.02np}{1000}.$$

At 25°, the temperature at which the measurements were made, $p = 23.52$. Inserting this value, we have

$$p_3 = 23.52 - 0.424n,$$

and for the complete formula,

$$p_2 = \frac{B_0 + \dfrac{h}{s} - p + 0.01802np}{\dfrac{2358.5 \text{ Cu}}{m\text{PV}} + 1},$$

or at 25°,

$$p_2 = \frac{B_0 + \dfrac{h}{s} - 23.52 + 0.424n}{\dfrac{2358.5 \text{ Cu}}{m\text{PV}} + 1}.$$

Gaus' formula was somewhat different. He found[1]

$$p_2 = \frac{\left(B_0 + \dfrac{h}{s}\right)^2}{\left(1 + 23.63\,\dfrac{Cu}{G}\right)\left(B + \dfrac{h}{s} + p\right)},$$

where G is the number of millimols of ammonia absorbed in the resistance cell. In our notation $G = \dfrac{mPV}{100}$, and therefore

$$p_2 = \frac{\left(B_0 + \dfrac{h}{s}\right)^2}{\left(1 + \dfrac{2363\,Cu}{mPV}\right)\left(B + \dfrac{h}{s} + p\right)}.$$

The discrepancy between the two coefficients 2363 and 2358.5 must be due to the fact that Gaus used for the atomic weight of copper a value other than 63.6. Further differences between the two formulas are caused by Gaus leaving out the volume of the water vapor in the right-hand member of the equation on p. 244, 11th line from above. With this correction introduced, his formula becomes identical with that given above. The two equations, however, give as they stand only slightly differing values for the vapor-pressure of the ammonia. The chief advantage of that derived by us consists in its much simpler form.

The corrections for the reduction of the barometric readings to $0°$ (B_0) were taken from Landolt and Börnstein's tables, p. 35.

The hydrochloric acid was prepared from sodium chloride and sulphuric acid, both chemically pure. The gas was received in water, the conductivity of which lay between 2×10^{-6} and 1.6×10^{-6}, and the acid used in the experiments was prepared from this supply by dilution with some of the same water. The acid in the resistance cell was approximately 0.01 normal, its exact strength being determined by its conductivity. For this purpose the conductivity for $\dfrac{1}{256}$,

[1] Ztschr. anorg. Chem., **25**, 244.

$\frac{1}{128}$, and $\frac{1}{64}$-normal acid at 25°, as given by Kohlrausch and Holborn (Leitvermögen der Elektrolyte, S. 167), were employed. The coefficients of a parabola passing through these three points and the origin were first calculated. This parabola, which probably coincides very closely within these limits, with the actual curve showing the relation of conductivity to concentration, has the formula

$$m = 2.5575k + 0.000146p - \frac{\sqrt{2.1316 + 3136.6k}}{10000}, \quad \text{(III.)}$$

where m is the concentration and k the corresponding conductivity.

This equation gives the strength of the acid at 18°. The acid being very dilute, we used as a correction in converting this value into normality at 25° merely the expansion of water alone for the same interval. The volume of the acid was measured in a specially constructed pipette (Fig. II.), which at 25° held 14.26 cc. This pipette was completely filled with the acid and then hung in the thermostat, with its mouth protected by a small tube and the cock closed. We were by this means always sure to use exactly the same volume of acid, independently of the temperature of the room.

The degree to which the acid is neutralized by the ammonia carried over, or P, is calculated from the conductivity, first of the pure acid and then of the partially neutralized solution. The experiment was allowed to proceed only until 70 to 80 per cent of the acid was neutralized, to avoid all possibility of some ammonia escaping absorption. As a check in this regard, a second receiver containing acid was occasionally attached to the cell. When the ex-

Fig. II.

periments were carried on as above, the conductivity of the acid in this second cell remained absolutely unchanged.
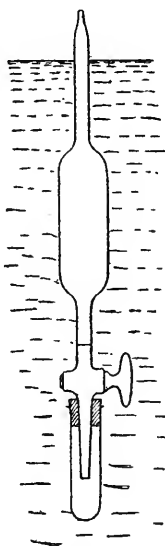
In order to determine the relation between the conductivity of the acid and the degree to which it was neutralized by ammonia, Gaus merely measured the conductivity of the former at stated intervals during the course of an experiment. He gives no data, but assumed from his results that the fall in conductivity was directly proportional to the amount of ammonium chloride formed. This relation, of course, is the very basis upon which all the experimental data depend. As the resistance is constantly increasing throughout the experiment, and owing to the fact that the change occurs, not uniformly, but in abrupt steps as the successive bubbles of gas enter the resistance cell, it seemed to us that this method was, to some degree, open to criticism. We ventured, therefore, to control his results by measuring the conductivity of an acid to which known quantities of ammonia had been added. To this end, a definite volume of acid was measured off, mixed with a known amount of ammonia which had been standardized against it, and after dilution to the proper extent the conductivity of the solution, at 25°, was determined. That of the acid alone, under the same conditions, was 0.004097, corresponding to an 0.01024 normal solution. The various measurements made are given in Table II.

Table II.

k.	P. Per cent.	P. cals. Per cent.	D. Per cent.
0.004097	0.00	—2.62	—2.62
0.002146	72.08	[72.08]	....
0.002100	73.89	73.84	—0.05
0.002047	75.90	75.87	—0.03
0.001927	80.42	80.46	+0.04
0.001703	89.04	[89.04]	....
0.001420	100.00	99.88	—0.12

Under P cals. are given the theoretical percentages of ammonium chloride required on the assumption that between P = 72.08 per cent and P = 89.04 per cent the conductivity curve is rectangular. Between these two values the coincidence is actually very good indeed. The equation of this line, which is

$$P = 154.24 - 38285k, \tag{IV.}$$

does not give a value for P when $k = 0.004097$ (P $= 0$) and is not very satisfactory for $k = 0.00142$ (P $= 100$). Although between the extremes in our experiments the equation holds good and can be used for the calculation of the degree of neutralization, therefore, it seems that Gaus' assumption is not wholly true.

In order to avoid the tedious necessity of preparing at intervals during the investigation a new acid solution of exactly the same conductivity as the above, a supply of about 2 liters was made, as occasion required, which had as nearly as possible the same concentration, and the value of P corresponding to the final conductivity was then subjected to a simple correction. To calculate the latter, the assumption was made that for very slight intervals of concentration the conductivity is directly proportional to the normality. While this is, of course, not true within wider limits, the error which it involves in our experiments may be entirely neglected. The limits of conductivity of all the acids used were 0.004097 and 0.004068. According to equation III., these figures correspond to the concentrations 0.010239 and 0.010164, respectively. On the basis of the above assumption the normality of the second acid would be $\frac{406.8}{409.7}$. 0.010239, or 0.010167. The difference between this value and 0.010164 is without significance for our purpose. Under the same conditions, the same assumption may be made in regard to an ammonium chloride solution.

If two acid solutions, of the molecular concentrations n_1 and n_3, and conductivities k_1 and k_3, respectively, be gradually neutralized by ammonia until they have become ammonium chloride solutions with the conductivities k_2 and k_4, the curves representing the involved changes of conductivity may be represented by I. and II., in Fig. III. Let k_P'' be the conductivity of the second acid, measured after it has been neutralized to P per cent by ammonia, and the corresponding, as yet unknown, conductivity of acid I. be k_P'. The two curves are not exactly parallel, but when the range of concentration of
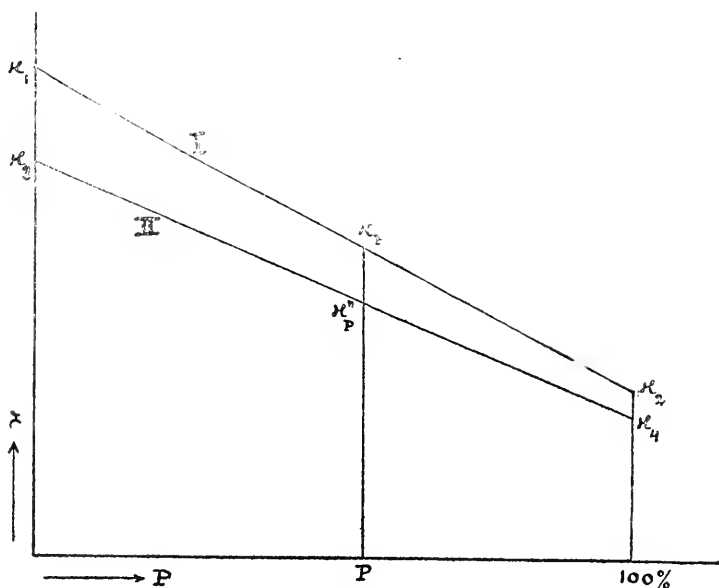
Fig. III.

the acids is very slight, they become approximately so, and
their eccentricity is in the same direction.   No noticeable er-
ror is introduced, therefore, in assuming the equation

$$k'_P = \frac{k''_P}{k_3}.k_1.$$

If we designate the resistance capacity of the cell by C, and
the resistances corresponding to the measured conductivities
k_3 and k''_P, by W_1 and W_P, respectively, then $k''_P = \dfrac{C}{W_P}$ and

$k_3 = \dfrac{C}{W_1}$, whence,

$$k'_P = \frac{W_1}{W_P}k.$$

By this equation the conductivity of an acid solution of the
original conductivity $k = 0.004097$, which has been neutral-
ized to very nearly the same degree, can be calculated, and
from this value the wished-for percentage of saturation esti-
mated by (III.).

The investigated ammoniacal copper solutions were prepared as follows : A pipette, of the construction shown in Fig. II., was filled, at 25°, from a supply of copper sulphate solution, the strength of which had been very accurately ascertained. This solution was run into a measuring-flask, and a measured quantity of a stock solution of ammonia then added from a calibrated burette. The proper quantity of water was then added and the temperature noted. The concentration of the ammonia was determined volumetrically, in a second portion of the stock solution, whenever a fresh mixture was prepared. The ammonia solutions used were prepared from the purest ammonium chloride and calcium hydroxide.

The normality of the total ammonia in the cupric solutions at 25° was calculated from the temperature of the solutions when prepared, and the expansion coefficients of the glass, the ammonia solution, and of the hydrochloric acid by which the latter was standardized. The expansion of the cupric ammoniacal solution was assumed to be the same as that of a pure ammonia solution of the same concentration. The correction for hydrochloric acid was obtained by interpolation between the values given by Schulze[1] for the normal acid and pure water. For the ammonia, the tables of Lunge and Wiernik[2] were used.

Experimental Results and Conclusions.

The first series of experiments was directed toward the question as to how far water solutions of ammonia follow Henry's law. Gaus assumed, from results of three experiments, which agreed only approximately with the theoretical, that the ratio between concentration and vapor-pressure of the ammonia is constant. The vapor-pressure was determined by us for five concentrations, varying from about 0.01 to 1 gram-molecule per liter. These preliminary results are given in Table III., and their graphic presentation in Curve I., Fig. IV.

[1] Ztschr. anal. Chem., **21**, 167.
[2] Ztschr. angew. Chem., 1889, 183.

Table III.

Molecular strength = n.	P_2. mm.	P_2 mean.	P_2 calculated.	Difference.
0.096	1.30	1.29	1.30	+0.01
"	1.27	....	....	....
0.242	3.25	3.23	2.27	+0.04
"	3.21	....	....	....
0.406	5.41	5.41	5.49	+0.08
"	5.41	....	....	....
0.729	9.80	9.80	9.86	+0.06
0.993	13.42	13.42	13.42	0.00
"	13.42	....	....	....
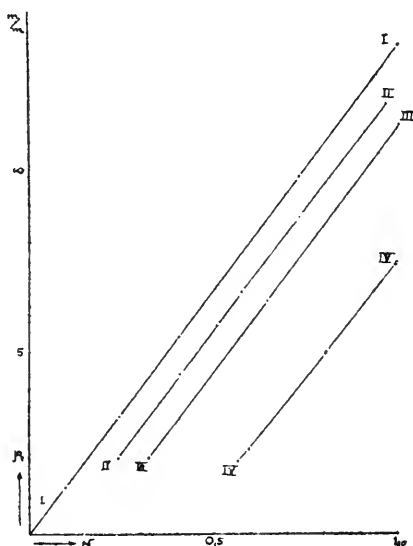
Fig. IV.

The equation of the line passing through the origin and the point $P_2 = 3.42$, $n = 0.993$ (Fig. IV.), is

$$P_2 = 13.52n.$$

The pressures at lower concentrations, as shown in the above table, are very considerably below the values calculated from this formula. The agreement is, nevertheless, much closer than was found by Gaus, as is seen from the following, in

which the theoretical values are calculated from his formula,
$P = 13.45n$.

n.	P_2.	Calculated.	Difference.
1.00	13.45	13.45	0.00
0.902	9.35	9.44	+0.09
0.456	5.97	6.13	+0.16

There can be no doubt, however, but that the law does not
hold strictly true. Our own results are expressed somewhat
more exactly by the quadratic equation

$$P_2 = 0.18n^2 + 13.34n, \qquad (V.)$$

from which the following values are obtained :

n	0.096	0.242	0.406	0.729	0.993
P_2	1.28	3.22	5.44	9.82	13.42
D	—0.01	—0.01	+0.03	+0.02	0.00

In the experiments on solutions containing copper, the
highest concentration of ammonia was, with one exception,
0.963 normal. The residual ammonia in these solutions, a
certain amount having been taken up to form the complex
salt, is much less than the original quantity, and in fact rarely
exceeded 0.70 normal. For ammonia solutions of concentra-
tion less than this, down to the lowest with which we experi-
mented, we can disregard this slight variation from the law.
Between these limits the equation

$$P_2 = 13.42n$$

gives very excellent results :

Table IV.

n.	P_2 calculated.	Difference.
0.096	1.29	0.00
0.242	3.25	+0.02
0.406	5.45	+0.04
0.729	9.78	—0.02

The variations here are only very slightly greater than
when the above quadratic equation is employed. For the
sake of showing more distinctly a certain parallelism between
the curves of the vapor-pressure of ammonia in water alone
and in presence of cupric sulphate, therefore, we have adopted

as the means of determining the concentration of the residual ammonia in the salt solutions the relation

$$P_2 = 13.42n.$$

The formula used for this purpose, accordingly, is

$$n_1 = \frac{P_2}{13.42},$$

n_1 being the concentration of the residual ammonia.

Ammoniacal Copper Solutions.—Experiments were made in two directions, the first being to ascertain how far the ratio of combined ammonia $(n-n_1)$ to copper varies with varying quantities of ammonia and a constant amount of copper, and the second, to find out the effect of varying concentration of the salt.

In the first series, a solution containing 0.0235 gram-molecule of copper sulphate was chosen, the ammonia varying in different experiments from a quantity barely sufficient to redissolve the cupric hydroxide at first formed, up to an approximately normal solution, in which the ratio of copper to total ammonia is about 1 : 40. Table V. contains the results, to which the curves II–II, Fig. IV., correspond.

Table V.—Cu = 0.0235.

n.	P_2 ohms.	Mean.	P_2 calculated.	Difference.
0.239	2.12	2.12	2.12	0.00
0.406	4.38	4.41	4.37	—0.04
"	4.44	....	....	....
0.508	5.72	5.73	5.73	0.00
"	5.73	....	....	....
0.575	6.65	6.66	6.63	—0.03
"	6.67	....	....	....
0.730	8.71	8.71	8.71	0.00
0.963	11.80	11.80	11.84	10.04

The vapor-pressure of the ammonia in these solutions is apparently very nearly directly proportional to its concentration. The calculated values for P_2 were obtained from the mean linear equation

$$P_2 = 13.41n - 1.08.$$

Now the curve of this equation is practically parallel to that

exerted in the more dilute aqueous solutions of ammonia alone. The difference between the two coefficients of n, 13.42 and 13.41, is hardly to be controlled by experiment. This indicates that, at least for concentrations of ammonia lying between 0.239 and 0.730 normal, the decrease in the pressure of ammonia, and consequently the amount of ammonia which has passed into combination with the copper, is constant for this concentration of the copper sulphate.

The following table gives the quantity of residual and combined ammonia in the various solutions. These values were calculated from the above mean equations :

Table VI.

n.	$Cu : n$.	n_1.	$Cu : n_1$.	Combined NH_3 $(n-n_1)$.
0.239	1 : 10.17	0.158	1 : 6.72	0.081
0.406	1 : 17.26	0.325	1 : 13.83	0.081
0.508	1 : 21.62	0.427	1 : 18.17	0.081
0.575	1 : 24.47	0.494	1 : 21.02	0.081
0.730	1 : 31.06	0.649	1 : 27.62	0.081
0.963	1 : 40.98	0.882	1 : 37.53	0.081

For ammonia of the concentration 0.882, the linear equation $P_2 = 13.42n$ is not strictly applicable, using the quadratic equation, the residual concentration, n, becomes in this case 0.879, and the combined, 0.084. In the other experiments, the combined ammonia when calculated by this equation ranges from 0.080, in the first, to 0.082, when $n = 0.730$. This very slight increase in the amount of combined ammonia is practically within the limit of error, but will be discussed at a later point.

The combined ammonia, 0.081 gram-molecule, stands to the copper in the ratio of 3.45 : 1. The fact that this molecular ratio remains constant even when the ratio of copper to total ammonia varies from 1 : 10 to 1 : 30, does not conform with Dawson and McCrae's observations. With virtually the same concentration of copper (Table I.) they found a variation of from 1 : 3.14, when Cu : total ammonia = 1 : 6 to 1 : 3.96, when Cu : total ammonia 1 : 16. We have found it impossible, however, to prepare a solution containing this amount of copper and only 6 molecules of ammonia. Solutions may

readily be prepared which are apparently clear, but after some time they deposit a dark-green, amorphous precipitate, which clings to the sides of the vessel, and is probably a highly basic salt. The amount of copper thus removed from the solution was in one case quantitatively determined. For this purpose, a solution containing 0.0235 gram-molecule copper and 0.1513 N ammonia, corresponding to the molecular ratio $Cu : NH_3 = 1 : 6.45$, was steadily shaken for two days at $25°$. On removal from the thermostat at the end of that time, a very considerable precipitate had formed. This was filtered off and the normality of the filtrate, with respect to copper, was determined in an aliquot portion. It proved to be only 0.0123 molecular, representing a loss of nearly 50 per cent by precipitation. Even when the ratio of $Cu : NH_3$ was $1 : 10$, evidence of slight double decomposition was obtained. The solution used in the first experiment (Table V.) showed with time a marked decrease in the vapor pressure of its ammonia. When freshly prepared, it gave for P_2 the value 2.12 mm., on the next day 2.05 mm., and on the third 1.98 mm. This can be explained only by the assumption that a soluble, or colloidal, basic salt and ammonium sulphate were gradually being formed.

The most probable complex formed by cupric copper and ammonia is certainly $Cu(NH_3)_4{}^{++}$. This is indicated by practically all experiments hitherto made in investigation of the subject. The fact that the amount of ammonia actually found to have passed into combination falls short of the amount which is required for the formation of this complex cannot be explained by the assumption that the solution contains two complexes, such as $Cu(NH_3)_4{}^{++}$ and $Cu(NH_3)_2{}^{++}$. In that case we could hardly expect the actual molecular ratio to be practically independent of the concentration of the residual ammonia. That it is so, our results very decidedly indicate. The assumption that the complex formed is $Cu_2(NH_3)_7{}^{++++}$, which would correspond roughly with the observed ratio, $Cu : NH_3 = 1 : 3.45$, is also hardly permissible, especially in the light of our subsequent experiments. If, then, the only complex formed is $Cu(NH_3)_4{}^{++}$, we must look

to physical causes to account for the very considerable differ-
ence between the observed decrease in the vapor-pressure of
the ammonia and that which is calculated for the formation
of this compound. The most plausible explanation, we be-
lieve, is found in the decreased solubility of ammonia in a
solution of the complex copper salt, as compared with its sol-
ubility in water. If this be true, the vapor-pressure of the
residual ammonia in the cupric solution would be higher than
that of the same amount in water, and the calculation of the
residual ammonia by the formula

$$n_1 = \frac{P_2}{13.42}$$

accordingly yield results which are too high. This assump-
tion is thoroughly in accord with the experiments hereafter to
be described.

Assuming that 4 molecules of ammonia combine with 1 of
copper, and that the amount of unaltered cupric ions, or of
copper sulphate, is inappreciable, the difference between this
quantity and that found by the vapor-pressure, as above, is
0.0235 (4.0—3.45), or 0.0129 gram-molecule per liter. This
seems, at first glance, to be very great, compared with the
concentration of the copper, but in reality it is about what
we should expect. The resemblance between the complex
metal-ammonia compounds and the salts of the alkali metals
is in many respects very striking. As has previously been
stated, Gaus found that the addition of 0.4 molecule of
potassium chloride to a normal solution of ammonia caused
an increase in the pressure of the latter about equal to the
vapor-pressure of 0.075 N. ammonia. If we calculate from
these data, by Jahn's formula,[1]

$$\frac{S-S_1}{M^{2/3}} = k,$$

the effect of 0.0235 molecule potassium chloride, the result
is almost the same as in the cupric solution, 0.012 gram-mole-
cule as compared with 0.0129 gram-molecule. In this for-
mula, S is the solubility of the gas in the pure solvent, S_1 its

[1] Ztschr. phys. Chem., **18**, 8 (1895).

solubility in the solution, and M the concentration of the dissolved salt.

By means of this formula we can find an approximate correction by which to obtain the true concentration of the residual ammonia, n_2. The constant k, which is given by the data of the above experiments, has the value 0.1588. For any concentration of copper, therefore,

$$+n_1 - n_2 = 0.1588M^{2/3},$$

in which n_2 is the true concentration. We have then,

$$n_2 = \frac{P_2}{13.42} - 0.1588M^{2/3}.$$

In solutions containing twice as much copper sulphate as was used in this series of experiments, or 0.047 molecule, this correction amounts to 0.021. The observed ratio of copper to combined ammonia should, therefore, be approximately $1 : 4 - \dfrac{0.021}{0.047}$, or $1 : 3.55$. This was confirmed by the following experimental results :

Table VII. Cu = 0.047.

n.	P_2.	Mean.	P_2 calculated.	Difference.
0.322	2.13	2.11	2.11	0.00
``	2.11	....	....	....
``	2.09	....	....	....
0.644	6.43	6.41	6.43	+0.02
``	6.39	....	....	....
1.000	11.25	11.23	11.21	—0.02
``	11.25	....	....	....

As would be expected from the above, we again find the decrease in vapor-pressure independent of the concentration of the ammonia. Under P_2 calculated stand the values derived from the mean equation

$$P_2 = 13.42n - 2.21,$$

the curve of which (III.—III., Fig. IV.), runs parallel to those obtained in the previous experiments

$$NH_3. \qquad\qquad P_2 = 13.42n ;$$
$$Cu = 0.0235. \quad P_2 = 13.41n - 1.08.$$

The results of this series of experiments, in respect to the amount of residual ammonia found, etc., are given in Table VIII. :

Table VIII.

n.	Cu : n.	n_1.	Cu : n_1.	$n-n_1$.
0.322	1 : 6.85	0.157	1 : 3.34	0.165
0.644	1 : 13.70	0.479	1 : 10.19	0.165
1.000	1 : 21.28	0.835	1 : 17.77	0.165

If the variation from Henry's law by ammonia be taken into consideration the residual ammonia, n_1, becomes respectively 0.158, 0.478, and 0.834, figures which differ only very slightly from the above. The molecular ratio of copper to combined ammonia, $\frac{n-n_1}{Cu}$, comes to 1 : 3.51, and the difference between this and 1 : 4, or 0.49 molecule ammonia, represents a concentration of 0.023 molecule per liter—the correction due to increased solubility in the salt solution. This agrees very closely with the calculated value for this correction, 0.021 molecule. Using the latter, we have for n_2 the value 0.186, and the molecular ratio Cu : NH_3 = 1 : 3.96.

These experiments, to a certain extent, confirm Gaus' conclusion that the lowering of the vapor-pressure of the ammonia by the addition of copper sulphate is directly proportional to the amount of the latter added. In our two experiments, the decrease is 1.08 mm. for 0.0235 Cu, and very slightly more than twice this amount, or 2.21 mm. for 0.047 Cu. Gaus found the decrease to be 2.49 mm. for 0.0491 Cu, and 5.02 mm. for 0.0982 Cu. His molecular ratios, 1 : 3.77 and 1 : 3.80, however, are somewhat higher than those observed by us.

In the next, and last, series of experiments the amount of copper sulphate added was five times as great as in the first series, or 0.1175 molecule. According to Jahn's formula, the decrease in the solubility should in this case be 0.038 gram-molecule, corresponding to 0.32 molecule copper. The observed ratio of copper to combined ammonia should, therefore, be 1 : 4 — 0.32, or 1 : 3.68. The experimental data are as follows :

Table IX. $Cu = 0.1175.$

n.	P_2.	Mean.	P_2 calculated.	Difference.
$\begin{pmatrix} 0.564 \\ \text{``} \end{pmatrix}$	$\begin{pmatrix} 2.02 \\ 1.99 \end{pmatrix}$	(2.01)	....	....
		....	....	....
0.596	2.35	2.33	2.38	—0.02
``	2.33	....	....	....
``	2.32	....	....	....
0.803	4.98	4.96	4.98	+0.02
``	4.94	....	....	....
0.804	5.03	5.02	5.00	—0.02
``	5.02	....	....	....
``	5.01	....	....	....
0.993	7.43	7.42	7.44	+0.02
``	7.44	....	....	....
``	7.38	....	....	....
0.995	7.50	7.48	7.46	—0.02
``	7.48	....	....	....
``	7.47	....	....	....
``	7.46	....	....	....

As in the previous series, the pressure is directly proportional to the concentration of the ammonia. The ratio of copper to combined ammonia, in these more concentrated solutions, however, is no longer quite constant, the mean equation of the pressure curve (IV.–IV., Fig. IV.), being

$$P_2 = 12.91n - 5.38.$$

This equation satisfies the above values of P_2 for all concentrations of ammonia except the first, 0.564. In this case the amount of residual ammonia, as compared with the copper, is far lower than in any previous instance, and it is probable that a basic salt had formed to a slight extent. The difference between the observed and calculated values of P_2 for this concentration was 0.11 mm. A solution containing less ammonia could not be prepared at all. Table X. contains the data calculated from the results of the other experiments.

Table X. $Cu = 11.75.$

n.	$Cu : n$.	n_1.	$Cu : n_1$.	$n - n_1$.	$\dfrac{n - n_1}{Cu}$.
0.596	1 : 5.07	0.171	1 : 1.46	0.425	3.62
0.803	1 : 6.83	0.371	1 : 3.16	0.432	3.68
0.804	1 : 6.84	0.372	1 : 3.17	0.432	3.68
0.993	1 : 8.45	0.554	1 : 4.71	0.439	3.73
0.995	1 : 8.47	0.556	1 : 4.73	0.439	3.73

Corrected for decreased solubility, the combined ammonia, $n - n_2$, and the molecular ratio $\dfrac{n - n_2}{\text{Cu}}$ become

$n - n_2$.	$\dfrac{n - n_2}{\text{Cu}}$.
0.463	3.94
0.470	4.00
0.470	4.00
0.477	4.05
0.477	4.05

The coincidence between these results and the theoretical is in general very good indeed. It cannot be doubted, however, but that the molecular ratio is not quite constant in these solutions in which the concentration of the copper is relatively great. The difference between the values found for the concentration of the residual ammonia in the first and last experiments, 0.014 molecule, is well outside the error of experiment, as it represents a vapor-pressure of 0.2 mm. We are disposed to ascribe this increase in the amount of combined ammonia to the formation, in a slight degree, of a higher complex, $Cu(NH_3)_5{}^{++}$ or $Cu(NH_3)_6{}^{++}$. The same phenomenon probably occurs, though only to a negligible extent, in the solutions which contain less copper, and this may be the cause of the slight increase in the molecular ratio observed, in the first series of experiments (Table VI.), in the solution containing 0.963 N. ammonia.

Even in the more concentrated solutions of this series the amount of the higher complex formed with 0.9905 N. ammonia is insignificant. If we assume its formula to be $Cu(NH_3)_6{}^{++}$, the increase in the molecular ratio from 1 : 3.94 to 1 : 4.05 means the passage of only 0.0035 gram-molecule, or about 3 per cent, of the copper into the higher complex. Whether the quantity formed is really directly proportional to the excess of ammonia, or not, cannot, of course, be determined in solutions of this strength, the concentration of the higher complex being too low. The investigation of more concentrated cupric solutions would probably throw at least enough light on the subject to tell us whether the second complex has

the formula $Cu(NH_3)_5^{++}$ or $Cu(NH_3)_6^{++}$. We regret that through an unfortunate circumstance we have been obliged to forego further research on the subject. It seems, probable, however, that $Cu(NH_3)_6^{++}$ is the compound more likely to result. This is indicated by the behavior of salts of nickel, so close an analogue of copper. A large number of nickel salts derived from the complex $Ni(NH_3)_6^{++}$ are known in the solid state, and can be crystallized from ammoniacal solutions, although Dawson and McCrae found that in nickel solutions, as in those of copper, less than 4 molecules of ammonia are absorbed to 1 of the metal.

The above experiments have been described in the order in which they were performed. For the sake of convenience in the development, therefore, the correction due to the decrease in the solubility of ammonia in water upon addition of cupric sulphate, was calculated from the results of the first series alone. The value assigned to it, as judged by the data of the subsequent experiments, is probably somewhat too low. Using the data of the second series, $Cu : NH_3 = 1 : 3.51$, as the basis of the calculation, we obtain

$$n_2 - n_1 = 0.1768M^{2/3}.$$

The mean between this coefficient and that which was used, 0.1588, is 0.1678, and this is probably very nearly correct. For the molecular ratio in the first two series, and in the first experiment in the third series, in which the observed ratio was the lowest, it yields :

$Cu = 0.0235$	$Cu : NH_3 = 1 : 4.03$
$Cu = 0.0470$	$Cu : NH_3 = 1 : 3.98$
$Cu = 0.1175$	$Cu : NH_3 = 1 : 3.95$

This coincidence satisfies the requirements of the theory advanced very well indeed.

Summary.

1. The molecular ratios between the copper and amount of combined ammonia in ammoniacal copper sulphate solutions, found by Dawson and McCrae, and others, can be explained only by one or two assumptions. Either two com-

plexes result or the difference between the ratio Cu : 4NH$_3$ and the observed ratio is due to the fact that the methods employed do not give the correct values for the residual concentrations of ammonia.

2. This second assumption is probably the true one. When the concentration of copper is low, the amount of ammonia which enters into combination, and hence the molecular ratio, is constant. For Cu = 0.0235, the ratio 1Cu = 3.45 NH$_3$ was found; for Cu = 0.0470, the ratio was 1Cu = 3.51 NH$_3$. This held true for all concentrations of ammonia between 0.239 and 0.729 molar in the first case and 0.322 and 1.000 molar in the second. This can be explained only on the theory that ammonia is less soluble in cupric sulphate solutions than in water, in which case the observed vapor-pressure in the salt solution gives too high values for the concentrations of the residual ammonia. The correction involved was calculated by Jahn's formula and found to equal 0.1678M$^{2/3}$, where M is the molecular concentration of the copper. Its value is about the same as that for ammonia in solutions of potassium chloride. With this correction the ratios in the two series become respectively

$$\text{Cu : NH}_3 = 1 : 4.03 \quad \text{and} \quad \text{Cu : NH}_3 = 1 : 3.98.$$

It must be assumed, therefore, that in solutions of this concentration all the copper passes into the complex Cu(NH$_3$)$_4^{++}$.

3. In solutions where the concentration of the cupric sulphate is 0.1175 molar, the same relation holds true when the excess of ammonia is not very high. The observed ratio of copper to combined ammonia was then 1 : 3.62, and the corrected ratio 1 : 3.95. With higher concentrations of the ammonia a small quantity of a higher complex, Cu(NH$_3$)$_5^{++}$ or Cu(NH$_3$)$_6^{++}$, forms, this amounting to about 3 per cent of the total copper when the concentration of ammonia is about normal.

Dr. Forssall's services were secured to me for the foregoing investigation through the generosity of the trustees of the Austin Fund of the Massachusetts Institute of Technology, who placed a very liberal grant at my disposal with which to

carry out the research. I wish to express to them my thorough appreciation of their assistance. J. L.

MASS. INSTITUTE OF TECHNOLOGY,
BOSTON, MASS., July, 1903.

REVIEWS.

JOURNAL DE CHIMIE PHYSIQUE : ELECTROCHIMIE, THERMOCHIMIE, RADIOCHIMIE, MÉCANIQUE CHIMIQUE, STOECHIOMÉTRIE. Publie par M. PHILIPPE A. GUYE, Professeur de Chimie à l'Université de Genève.

The appearance of this new journal of physical chemistry in French will undoubtedly mark a new epoch for this subject in France. Certain chapters in physical chemistry owe their existence largely to the work of French chemists. We should mention especially the work of Raoult on the lowering of the freezing-point and vapor-tension of solvents by dissolved substances, that of Berthelot on thermochemistry, of Pasteur on optical activity, of Guye on the effect of changing the masses of the atoms or groups on optical activity, of Le Chatelier on chemical equilibrium, and many other investigations of great importance to physical chemistry have come from those who read most easily the French language.

The present journal will bring the subject as a whole more closely home to the French chemists, and we may fairly expect from them renewed activity in this field.

Prof. Guye can be heartily congratulated upon his efforts to establish the new journal, which we hope may prove to be an honor to its subject, as well as to its country and editor.

H. C. J.

A PHYSICO-CHEMICAL REVIEW. A Complete International Review of the Sciences of Physical Chemistry, and the Allied Branches of Chemistry and Physics. Edited by DR. MAX RUDOLPHI, Darmstadt.

The journal in question is not to be an organ for the final publication of original investigations, but a '' comprehensive, centralizing review of progress in physical chemistry.'' The journal is to be distinctively international in character, and is to include English, French, and German abstracts. It is the desire of the editor that the abstracts should be prepared, whenever possible, by the authors of the papers, and will be published immediately after the publication in other journals of the original papers. The journal aims to cover the entire field of general or physical chemistry, and also to include those publications in chemistry and physics which have any physical chemical bearing.

It is obvious from this sketch that the new '' Review'' aims to bring physical chemical literature together in a manner not done at present by any other journal. It will doubtless contribute its share to the development of this growing branch of science, and we wish it the very best success.   H. C. J.

QUANTITATIVE CHEMICAL ANALYSIS. Adapted for use in the Laboratories of Colleges and Schools. By FRANK CLOWES, D.Sc., London, Emeritus Professor of Chemistry in the University College, Nottingham, and J. BERNARD COLEMAN, A.R.C.Sc., Dublin, Professor of Chemistry in the Southwestern Polytechnic, Chelsea, S. W. Sixth Edition. Philadelphia : F. Blakiston's Son & Co. 1903. pp. xxiv + 602. Price, $3.50 net.

The present edition differs from that issued in 1900 by the addition to the appendix of a description of the procedure of Landsberger, as modified by Walker and Lumsden, for the determination of molecular weights by the rise of boiling-point of solutions, a procedure for the analysis of aluminium alloys, a description of the Soxhlet condenser, and a table of four-place logarithms. The description of the estimation of cyanide by means of iodine is omitted. The authors state that the entire text has been subjected to revision. This, however, apparently relates to minor details, with the exception of the changes above noted.

The subject-matter of the volume is well arranged for teaching purposes and is indexed with unusual care and thoroughness. The statements regarding preliminary operations and the pre-requisites for successful quantitative work are forceful and clear. These are followed by descriptions of a considerable variety of gravimetric determinations, including about forty elements or radicals. Typical volumetric processes are the subject of the third large division of the book, while in Part IV. both gravimetric and volumetric processes are applied to a wide range of materials of technical importance, to methods of analysis of waters, food-stuffs, soaps, and tanning materials, and to methods of ultimate organic analysis. Part V. deals with the analysis of gases, Part VI. contains tables for reference, and Part VII. and the appendix include supplementary information useful for the analyst.

It is difficult to properly define the scope of a manual of quantitative analysis after it has passed the bounds of an introductory treatise. The authors, in this instance, have avowedly limited themselves to the presentation of procedures which have given satisfactory results in their laboratories, and they have also appended a list of works of reference upon general and special lines of analysis. This, of course, largely disarms criticism of their selection of methods since it is im-

possible to determine to what extent the pupil is made to understand that he should, in his post-graduate experiences, look about for other methods than those given in this volume before making a final choice of procedure for his work in hand. Yet one cannot help wondering, for instance, why, when so much is said of the color-test for the determination of carbon in irons and steels, no mention is made of the color-test for manganese, or of the rapid volumetric methods for manganese or phosphorus among methods which are represented as typical of those in general use for the analysis of this class of material. The absence of the Lunge method for the determination of sulphur in pyrites is also noteworthy.

The list of works and journals for reference is restricted to those in English, and essentially to those published in England. As the average student has too strong a tendency, at best, to confine his reading to his own language and country, and to feel that time devoted to the acquisition of a foreign language is but ill-spent, the entire omission of reference to works in French or German (and possibly to American chemical journals as well) seems to foster that tendency.

No reference is made to the ionic theory of its applications, and the statements of the principles underlying the vapor-density determinations are very brief.

Whatever differences of opinion may, and inevitably will, be held regarding the selection of individual methods of analysis, the fact that the present is the sixth edition of this work in twelve years is adequate indication that it has deservedly made many friends.   H. P. T.

DIE KONSTITUTION DES KAMPHERS UND SEINER WICHTIGSTEN DERI-VATE. Die theoretischen Ergebnisse der Kampherforschung monographisch dargestellt von OSSIAN ASCHAN. Verlag von Fr. Vieweg und Sohn, Braunschweig. One vol., pp. xi + 117. 1903. M. 3.50.

Camphor is one of the first chemical individuals of an organic nature known to chemists. Its medical, ritualistic, and commercial history added to the interest of this natural product from the Orient. It, therefore, attracted the attention of chemists even before organic chemistry began to develop as a distinct branch of our science. It even gave its name to an entire group of natural and artificial compounds, yet for more than a hundred years its own molecule remained a mystery to the investigators of all civilized countries who tried to unravel its constitution. In recent decades, chemists not especially engaged in the study of camphor and its derivatives could no longer hope to follow the work of the small army of investigators in this field. The monograph of Aschan, therefore, will

be very welcome to all who desire light on this interesting subject.

After a brief historical introduction, the author discusses not less than thirty-three structural formulas proposed for camphor. He then presents twelve definite structural conclusions based on experiment which bear upon the arrangement of the atoms in the camphor molecule. In a fourth chapter he submits the camphor formulas, presented in the second chapter, to a careful scrutiny in the light of these twelve corollaries, as they may be called, and comes to the conclusion that the Bredt formula alone is in harmony with all, while it is the only one which admits of a satisfactory explanation of the conversion of camphor to symmetrical camphene. The keystone of this arch of corollaries, the satisfactory synthesis of camphor, is still wanting.

The remaining chapters are devoted to further "Abbau" products of camphor and to the constitution of camphene and bornylene.

Aschan's monograph is certainly a unique volume in modern chemical literature. The author has done well to exclude all descriptions of substances and processes from this speculative account. These are to be included in a larger work covering all alicyclic compounds, soon to be published. E. K.

THERMODYNAMICS AND CHEMISTRY. A Non-mathematical Treatise for Chemists and Students of Chemistry. By P. DUHEM, Correspondant de l'Institut de France, Professor of Theoretical Physics at the University of Bordeaux. Authorized translation by GEORGE R. BURGESS, Docteur de l'Université de Paris, Instructor in Physics, University of California. New York : John Wiley & Sons; London : Chapman & Hall, Limited. 1903. pp. 445.

The author is greatly impressed with the importance of thermodynamics for the chemist. This is seen from his own words taken from his preface : "The laws formulated by thermodynamics impose a rational order upon the most confused chapters of chemistry ; a few simple, clear rules bring order out of what was a chaos ; the circumstances under which the various reactions are produced, the conditions which stop them and assure chemical equilibrium, are fixed by theorems of a geometrical precision." "What the chemist expects above all from thermodynamics are simple, clear rules, easy to use, which shall serve him as conducting threads through the fruitful labyrinth of chemical facts already known, which shall guide him in the course of his researches, which shall show him exactly, for every reaction, the variable conditions at his disposal and the essential conditions which he is held to determine."

The author is greatly impressed with the depth and value of the work of that distinguished American physicist, J. Willard Gibbs, and his work shows the imprint of this master at every stage.

The contents of this excellent book can be judged best by a brief reference to the headings of the twenty chapters of which it is composed. They are : Work and Energy, Quantity of Heat and Internal Energy, Chemical Colorimetry, Chemical Equilibrium and the Reversible Transformation, The Principles of Chemical Statics, The Phase Rule, Multivariant Systems, Monovariant Systems, Multiple or Transition Points, Displacement of Equilibrium, Bivariant Systems—The Indifferent Point, Mixed Crystals—Isomorphous Mixtures, Critical States, Chemical Mechanics of Perfect Gases, Capillary Actions and Apparent False Equilibrium, Genuine False Equilibrium, Unequally Heated Spaces and Chemical Dynamics and Explosions.

The work as a whole may be said to be a sign of the times, and an indication of what the chemistry of the future will be. Every such contribution to the literature as the one in hand will contribute to this end.

The work of the translator seems to have been faithfully done. The only fault that we can find is that the translation is in places too literal. In the preface we find such statements as " this opposition has been *exposed* with very great clearness," " the work in which I have tried to *expose*, etc," " we have accompanied each of them with numerous examples." These are, after all, comparatively small matters, and any one who has any appreciation of the drudgery involved in translating a work of any size will feel thankful to Dr. Burgess for making this book accessible to English-speaking students. It is to be hoped that the book will receive the attention that it deserves.   H. C. J.

AMERICAN

CHEMICAL JOURNAL

ON THE NATURE OF CONCENTRATED SOLU-TIONS OF ELECTROLYTES—HYDRATES IN SOLUTION.

BY HARRY C. JONES AND FREDERICK H. GETMAN (CARNEGIE RESEARCH ASSISTANT).[1]

The present investigation is a continuation of the work that was begun in this laboratory by Jones and Chambers[2] in 1900. It had been observed by Jones and Ota[3] and by Jones and Knight[4] in connection with their work on the condition of double sulphates, chlorides, nitrates, cyanides, etc., in aqueous solution, that concentrated solutions of these substances frequently show abnormally great depression of the freezing-point of water. The first systematic study of this problem was made by Jones and Chambers.[5] They determined the molecular lowering produced by solutions of calcium chloride ranging in concentration from 0.102 to 0.612 normal. Similarly, they determined the molecular lowering produced by strontium chloride from 0.05 to 0.75 normal; by barium chloride from 0.0976 to 0.5858 normal; by magnesium chloride from 0.0508 to 0.6099 normal; by cadmium chloride from

[1] Dr. Getman was appointed Carnegie Research Assistant in October, 1903. The continuation of this investigation was, therefore, made possible by a grant from the Carnegie Institution.

[2] This JOURNAL, **23**, 89 (1900).

[3] *Ibid.*, **22**, 5 (1899).

[4] *Ibid.*, **22**, 110 (1899).

[5] *Loc. cit.*

0.214 to 1.072 normal; by calcium bromide from 0.04355 to 0.5226 normal; by strontium bromide from 0.052 to 0.621 normal; by barium bromide from 0.10 to 0.5 normal; by magnesium bromide from 0.0517 to 0.517 normal; by cadmium bromide from 0.22 to 0.88 normal.

With every salt studied, except cadmium chloride and bromide, the molecular lowering decreased with the concentration up to a certain point, and then increased as the concentration increased. In a word, there was a well-defined minimum in the curve expressing the relation between molecular lowering of the freezing-point and concentration of the solution.

The conductivities of these solutions increased regularly with the dilution, from the most concentrated to the most dilute solution, there being no indication of a minimum in any of the conductivity curves.

The work begun by Jones and Chambers was continued in this laboratory by Chambers and Frazer.[1]

They studied solutions of hydrochloric and phosphoric acids, of strontium and cadmium iodides, of sodium acetate, copper sulphate, and zinc chloride, in the same manner and approximately over the same range of concentration as had been done by Jones and Chambers. They found a more or less well-defined minimum in the freezing-point curve for every one of the above substances.

Somewhat more than two years ago we took up an extended investigation in this field, intending to study especially solutions of very great concentration. In all of the previous work the ordinary Beckmann thermometers, covering a range of 5° or 6°, had been used. It is obvious that these could not be employed for very concentrated solutions. We had two thermometers of the Beckmann type constructed, one having a range of 12° and graduated to fiftieths of a degree, the other having a range of 25° and graduated to twentieths of a degree. The latter was used for the most concentrated solutions, while the former was employed with solutions of lesser

concentration, but still too concentrated to admit of the use of an ordinary Beckmann thermometer.

When the first part of our investigation was well under way a paper along the same general line was published by W. Biltz.[1] It surprised us that he should have entered this field at the time named, since Jones and Chambers and Jones and Frazer had stated in both papers that this line of investigation, which had been taken up systematically for the first time in this laboratory, would be continued here and pushed forward as rapidly as possible.

Biltz worked with sodium, potassium, ammonium, caesium, rubidium, lithium, mercuric, cupric, zinc, manganous, nickel, cobalt, and ferrous chlorides ; potassium, lithium, aluminium, and cupric bromides ; potassium and lithium iodides ; potassium fluoride, potassium cyanide, potassium sulphocyanate, and lithium nitrate.

All of the above substances showed well-marked minima in the freezing-point curves, except potassium, lithium, and rubidium chlorides ; potassium and aluminium bromides ; lithium iodide, potassium cyanide, and potassium sulphocyanate.

Since the work of W. Biltz did not extend to any very great concentration, and the data which we had already obtained showed that this was the interesting and really important field to study, we did not modify our plans in the least because of the work that W. Biltz had done.

We, however, thought it advisable to publish some of the data which we had obtained at that time,[2] to indicate again the line along which we were working, and to avoid any duplication of work in the future.

The first part of our investigation has recently been published in full.[3] The compounds studied were hydrochloric acid, lithium chloride, ammonium chloride, sodium chloride, potassium chloride, calcium chloride, strontium chloride, barium chloride, nitric acid, lithium nitrate, ammonium nitrate, sodium nitrate, potassium nitrate, sulphuric acid, am-

[1] Ztschr. phys. Chem., **40**, 185 (1902).

[2] This JOURNAL, **27**, 433 (1902).

[3] Ztschr. phys. Chem., **46**, 244 (1903). Phys. Rev., **18**, 146 (1904).

monium sulphate, sodium sulphate, potassium sulphate, sodium carbonate, potassium carbonate, phosphoric acid, primary potassium phosphate, sodium hydroxide, and potassium hydroxide.

The freezing-point, conductivity, and refractivity of a number of solutions of these substances were measured, and in some cases the boiling-points were also determined. A few of the more interesting results that were obtained in concentrated solutions are given below. Table I. is for hydrochloric acid.

m = concentration in gram-molecular normal

s = observed depression of the freezing-point.

k = correction for change in concentration due to separation of ice.

Δ = corrected depression of the freezing-point.

$\dfrac{\Delta}{m}$ = molecular depression of the freezing-point.

Hydrochloric Acid (see Fig. I.).

m.	s.	k.	Δ.	$\dfrac{\Delta}{m}$.
1.0	4.140	0.018	4.122	4.122
1.5	6.720	0.087	6.633	4.422
2.0	10.218	0.281	9.937	4.969
2.5	13.510	0.055	13.455	5.382
3.0	18.100	0.004	18.096	6.030

The conductivity measurements are tabulated in the usual manner; v is the volume of the solution, or the number of liters that contain a gram-molecular weight of the electrolyte, and $\mu_v 0°$ = the molecular conductivity at 0°—the temperature the nearest comparable with those at which the freezing-point measurements were made, at which $\mu\infty$ could be determined.

v.	$\mu_v 0°$.	v.	$\mu_v 0°$.
2.0	216.50	0.500	170.19
1.0	200.32	0.400	152.38
0.667	182.35	0.333	141.87

The value of $\mu\infty$ for hydrochloric acid at 0°, from the work of Jones and Douglas,[1] is 240.6. Knowing this value, we can

[1] This JOURNAL, **26**, 434 (1901).

calculate the dissociation of each of the above solutions. The
values are :

v.	Dissociation *a.* Per cent.	*v.*	Dissociation *a.* Per cent.
2.000	90.0	0.500	70.7
1.000	83.3	0.400	63.3
0.667	75.8	0.333	58.9

The most concentrated solution of hydrochloric acid that
was studied was dissociated only about 59 per cent, and yet
showed a molecular lowering of the freezing-point of 6.03.

If hydrochloric acid—a binary electrolyte—was completely
dissociated it would give a molecular lowering of only $1.86 \times 2 = 3.72$. Being about 60 per cent dissociated, the molecu-
lar lowering would be calculated thus:

$$i - 1 = \alpha$$
$$\alpha + 1 = i$$

In this case $i = 1.60$.

But
$$\frac{\text{mol. lowering}}{1.86} = i.$$

Molecular lowering $= 1.86 \times 1.60 = 2.97$.

The difference between, in round numbers, 3 and 6, is the
magnitude of the apparent abnormality in the freezing-point
lowering, as shown by a three-normal solution of hydrochloric
acid.

Our theory to account for this and all similar phenomena is
that in concentrated solutions there is combination between
the solvent and dissolved substance, thus removing from the
field of action, as far as freezing-point lowering is concerned,
a part of the solvent, in reality, concentrating the solution by
just so much.

We cannot calculate accurately the number of molecules of
water in combination in any solution with 1 molecule or ion
of the dissolved substance, unless we know the specific grav-
ity and concentration of the solution, which would tell us just
how much water was present in a liter of that solution. We
propose to take up this side of the question a little later, and
calculate for many of the solutions studied the exact number

of molecules of water combined with 1 molecule of the dissolved substance. However, from data already at hand, we can say that in a three-normal solution every molecule of hydrochloric acid, dissociated or undissociated, is combined with about 8 molecules of water.

Before leaving hydrochloric acid, it should be pointed out, that, while there is a minimum in the freezing-point curve at about 0.1 normal, the conductivity curve shows no sign of a minimum, in this or any other region that has been studied.

Turning to sulphuric acid, the following data were obtained :

Sulphuric Acid (see Fig. I.).

m.	s.	k.	Δ.	$\dfrac{\Delta}{m}$.
0.10	0.413	0.016	0.397	3.970
0.30	1.180	0.024	1.156	3.853
0.50	2.040	0.023	2.017	4.034
1.00	4.203	0.014	4.189	4.189
1.50	7.450	0.007	7.443	4.962
2.00	11.300	0.004	11.296	5.648
2.50	16.275		16.275	6.510

v.	$\mu_v 0^\circ$.	v.	$\mu_v 0^\circ$.
2.000	277.30	0.333	155.29
1.000	253.44	0.286	135.00
0.667	221.25	0.250	118.86
0.500	199.42	0.222	100.21
0.400	178.79	0.200	86.97

The dissociation of the above solutions of sulphuric acid at 0° can be readily calculated. Jones and Douglas[1] determined the value of $\mu\infty$ for sulphuric acid at zero, and found it to be 500. The dissociations of the above solutions of sulphuric acid are :

v.	α.	v.	α.
	Per cent.		Per cent.
2.000	55.46	0.333	31.06
1.000	50.69	0.286	27.00
0.667	44.25	0.250	23.77
0.500	39.88	0.222	20.04
0.400	35.76	0.200	17.39

[1] This JOURNAL, **26**, 428 (1901).

Take the twice normal solution of sulphuric acid ; it is dissociated only 17.4 per cent, and gives a molecular lowering of the freezing-point of water of 5.648. The molecular lowering would be calculated from the dissociation as follows, sulphuric acid being a ternary electrolyte :

$$\alpha = \frac{i-1}{2} \; ;$$

$$i = 1.348 \; ;$$

$$\frac{\text{Molecular lowering}}{1.86} = i = 1.348.$$

Molecular lowering $= 2.50$.

In a manner similar to that employed in the case of hydrochloric acid we can calculate approximately the number of molecules of water combined with 1 molecule of sulphuric acid in a twice-normal solution of the acid. We find it to be about 14 molecules.

There are two other substances that were studied in this earlier work, which should be briefly mentioned in this connection, on account of the very large lowering of the freezing-point of water produced by them. They are calcium chloride and strontium chloride.

Calcium Chloride (see Fig. I.).

m.	*s.*	*k.*	Δ.	$\frac{\Delta}{m}$.
0.05				4.85
0.10		.		4.98
0.20				4.96
0.30				5.02
0.40				5.16
0.50				5.26
1.00	6.350	0.005	6.345	6.345
1.50	11.300	0.004	11.296	7.531
2.00	17.875	0.008	17.867	8.934

v.	$\mu_v 0°$.	*v.*	$\mu_v 0°$.
1.000	71.16	0.500	53.98
0.667	62.14	0.400	44.79

Strontium Chloride (see Fig. I.).

$m.$	$s.$	$k.$	$\Delta.$	$\frac{\Delta}{m}.$
0.05				5.16
0.10				4.88
0.20				4.87
0.30				4.90
0.40				4.95
0.50				5.09
1.00	6.010	0.010	6.000	6.000
1.5	10.725		10.725	7.150
2.0	16.425	0.003	16.422	8.211

$v.$	$\mu_v 0°.$	$v.$	$\mu_v 0°.$
2.000	84.27	0.667	63.01
1 000	74.57	0.500	55.26
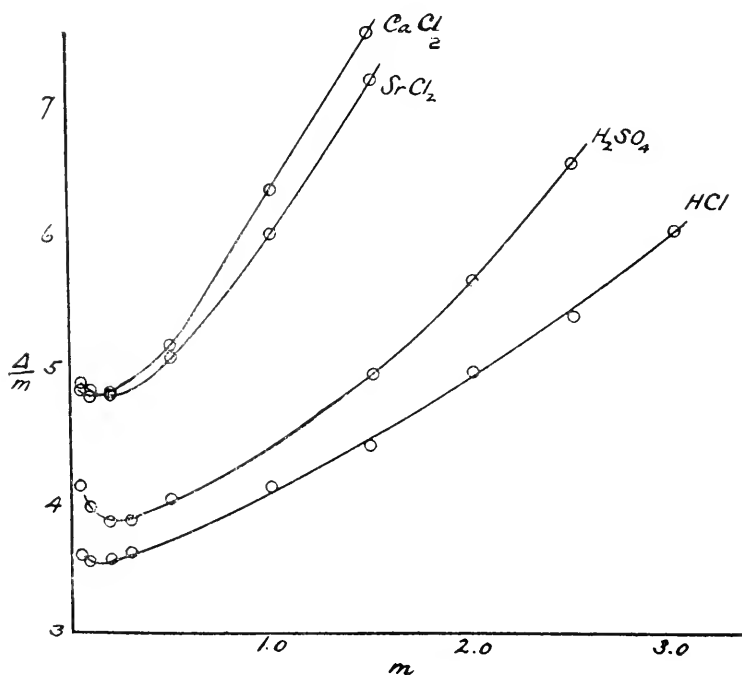
Fig. I.

The double-normal solutions of these chlorides are dissocia-
ted, probably, about 30 per cent. We shall determine this

accurately a little later. On this basis the molecular lowering produced by a twice-normal solution of calcium chloride would be 3.0, while the lowering actually found was 8.9. This, corrected for specific gravity, would show that each molecule of calcium chloride was combined with about 19 molecules of water in a double-normal solution. Each molecule of strontium chloride would be combined with 1 or 2 molecules less.

Of the compounds studied in this earlier work, all except sodium nitrate, potassium nitrate, the sulphates of sodium, potassium, and ammonium, and primary potassium phosphate show a minimum in the freezing-point curves, and from this minimum the molecular lowering increases with the concentration as well as with the dilution.

All of the twenty-two substances studied in this part of the investigation gave conductivity curves which are perfectly normal, showing no irregularities whatever in the region where the minimum of molecular depression manifests itself ; the molecular conductivity increasing regularly with the dilution. The refractivity curves also show no irregularities at any point, being for the most part nearly straight lines.

The boiling-point curves obtained in this part of the work also show minima, analogous to the freezing-point curves. Since more accurate boiling-point determinations will be recorded later in this paper, a fuller discussion of this subject will appear further on.

The discussion of the meaning of these various curves will be reserved until later in this paper.

Second Part of This Investigation.

The above investigation was extended to fifteen compounds, and the prime object of this paper is to record the results obtained. These are : Manganese chloride, manganese sulphate, manganese nitrate, nickel chloride, nickel sulphate, nickel nitrate, cobalt chloride, cobalt sulphate, cobalt nitrate, cupric chloride, copper sulphate, cupric nitrate, aluminium chloride, aluminium sulphate, and aluminium nitrate.

In the tables given below the symbols have the following significance :

In '' Freezing-point Measurements,'' m is the concentration in terms of gram-molecular normal, Δ the corrected lowering of the freezing-point, and $\dfrac{\Delta}{m}$ the molecular lowering.

In '' Conductivity Measurements,'' v is the volume of the solution, or the number of liters that contain a gram-molecular weight of the electrolyte.

Under '' Refractivity Measurements'' m is the concentration in terms of gram-molecular normal, λ the reading on the Pulfrich refractometer, and n the index of refraction.

Manganese Salts.

The results with the manganese salts are recorded in Tables I. to IX., and the results are plotted in Figs. II. to IV.

Manganese Chloride,
MnCl$_2$,—125.9.

Table I.—Freezing-point Measurements.

m.	Δ.	$\dfrac{\Delta}{m}$.
0.053	0.255	4.81
0.106	0.508	4.79
0.133	0.639	4.80
0.266	1.259	4.73
0.400	2.004	5.01
0.532	2.790	5.24
0.796	4.247	5.34
0.902	4.825	5.36
1.061	5.965	5.62

Table II.—Conductivity Measurements.

v.	μ_v.	v.	μ_v.
18.87	88.67	1.88	65.16
9.43	81.81	1.26	57.32
7.51	79.85	0.94	51.44
3.76	73.49		

Table III.—*Refractivity Measurements.*

m.	λ.	n.
0.053	67° 7′	1.32656
0.106	66° 53′	1.32766
0.133	66° 45′	1.32829
0.266	66° 5′	1.33150
0.533	64° 50′	1.33768
0.796	63° 40′	1.34363
0.902	63° 14′	1.34588

Manganese Nitrate,
$Mn(NO_3)_2$—179.08.

Table IV.—*Freezing-point Measurements.*

m.	Δ.	$\frac{\Delta}{m}$.
0.035	0.090	2.56
0.18	0.410	2.25
0.35	0.841	2.40
0.53	1.297	2.44
0.87	2.184	2.51
1.05	2.748	2.61
2.10	6.310	3.05
2.80	9.315	3.33
3.50	12.690	3.63

Table V.—*Conductivity Measurements.*

v.	μ_v.	v.	μ_v.
28.6	49.18	0.95	33.35
5.56	44.33	0.47	29.10
2.85	41.79	0.36	24.49
1.89	39.60	0.29	21.95
1.15	36.80		

Table VI.—*Refractivity Measurements.*

m.	λ.	n.
0.035	67° 20′	1.32554
0.18	66° 55′	1.32751
0.35	66° 30′	1.32949
0.53	66° 4′	1.33142
0.87	65° 15′	1.33643
1.05	64° 50′	1.33768
2.10	62° 30′	1.34974
2.80	61° 5′	1.35734
3.50	59° 44′	1.36459

Manganese Sulphate,
$MnSO_4$—151.06.

Table VII.—*Freezing-point Measurements.*

m.	Δ.	$\frac{\Delta}{m}$.
0.08	0.194	2.43
0.16	0.354	2.21
0.25	0.510	2.04
0.33	0.676	2.04
0.41	0.792	1.94
0.82	1.556	1.90
0.98	1.898	1.93
1.31	2.701	2.06
1.64	3.668	2.23

Table VIII.—*Conductivity Measurements.*

v.	μ_v.	*v.*	μ_v.
12.5	52.78	1.22	26.29
6.25	44.48	1.02	23.70
4.00	38.35	0.76	19.50
3.03	35.65	0.61	16.20
2.50	34.25		

Table IX.—*Refractivity Measurements.*

m.	λ.	*n.*
0.08	66° 55′	1.32750
0.16	66° 28′	1.32965
0.25	66° 5′	1.33150
0.33	65° 39′	1.33362
0.41	65° 16′	1.33575
0.82	63° 19′	1.34545
0.98	62° 35′	1.34930
1.31	61° 13′	1.35661
1.64	59° 57′	1.36357

The chloride shows a minimum in the molecular lowering at
about 0.2 normal ; the minimum for the nitrate is at a slightly
greater concentration, while the sulphate does not show the
freezing-point minimum until a concentration of about 0.8
normal is reached. The positions of these minima are clearly
seen in Fig. II. The molecular lowering of manganese chlo-
ride is about 5.6 at normal concentration, while the molecu-
lar lowering of manganese nitrate at 3.5 normal is only 3.6.

The molecular lowering produced by manganese sulphate at normal concentration is less than 2. Similar relations will appear when the salts of other heavy elements are compared, the sulphates in general showing much smaller lowerings of the freezing-point than the chlorides and nitrates.
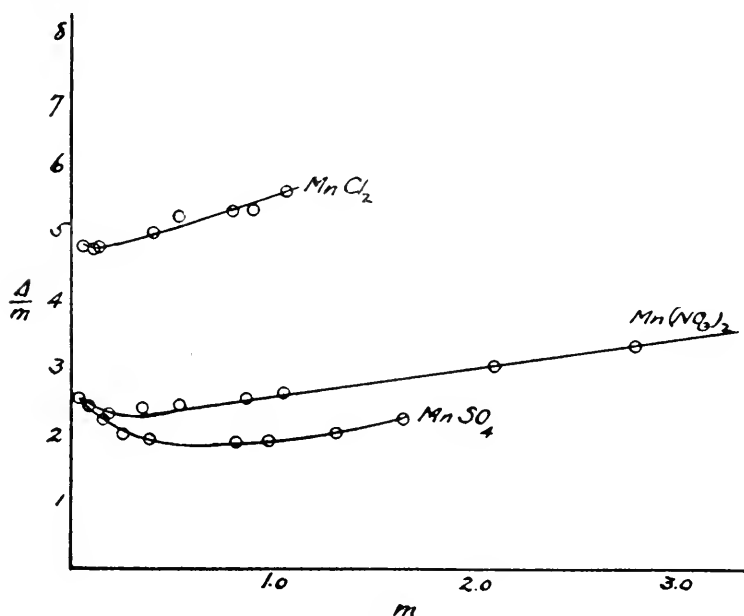
Fig. II.
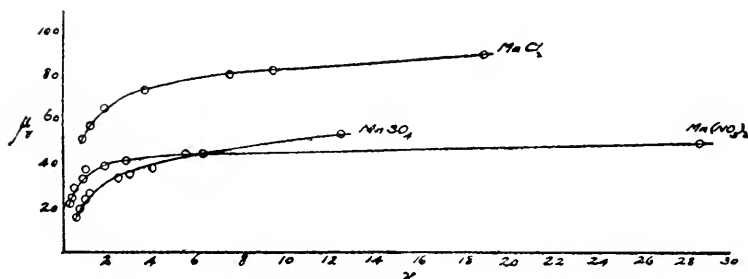
Fig. III.
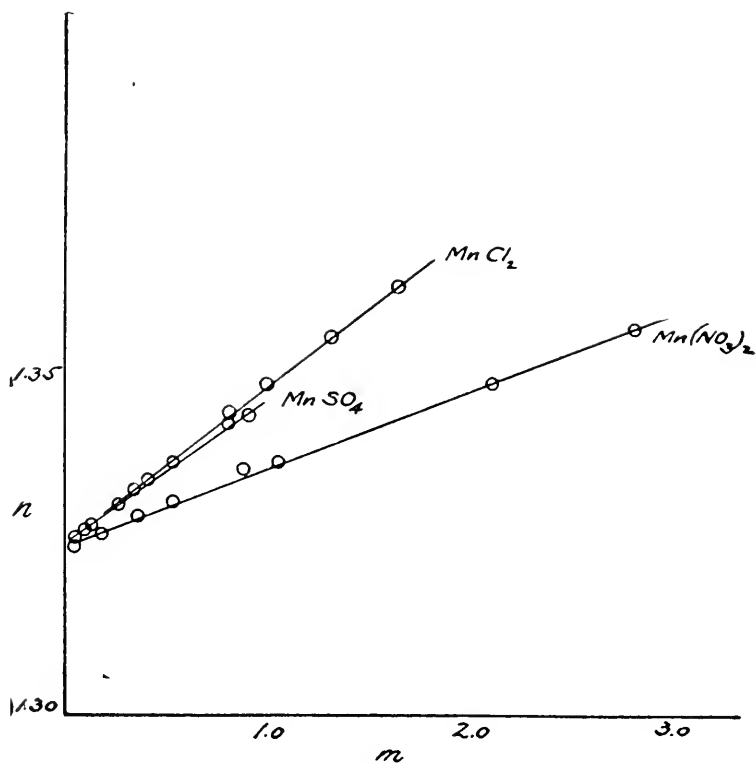
Fig. IV.

The molecular conductivities of all these salts increase regularly with the concentration, as can be seen in Tables II., V., and VIII., and in Fig. III. There is no sign of a minimum in the conductivity curves at any dilution used in this investigation. The refractivity data (Tables III., VI., and IX.) show that the index of refraction, for all three manganese salts, increases with the concentration. When these data are plotted as curves, the concentrations as abscissæ, and the indices of refraction as ordinates, the curves are very nearly straight lines. The complete absence of minima is therefore obvious.

Salts of Nickel.

The results with the salts of nickel are recorded in Tables

X. to XVIII., and the results are plotted in Figs. V. to VII.

Nickel Chloride,
$NiCl_2$—129.6.

Table X.—*Freezing-point Measurements.*

m.	Δ.	$\frac{\Delta}{m}$.
0.037	0.205	5.54
0.074	0.380	5.11
0.149	0.768	5.15
0.223	1.170	5.25
0.297	1.585	5.34
0.372	2.032	5.46
0.446	2.458	5.51
0.521	2.945	5.65
0.743	4.547	6.12

Table XI.—*Conductivity Measurements.*

v.	μ_v.	v.	μ_v.
27.0	103.2	2.68	77.9
13.5	97.0	2.24	77.2
6.7	88.64	1.92	75.2
4.48	85.50	1.35	70.23
3.38	82.52		

Table XII.—*Refractivity Measurements.*

m.	λ.	n.
0.037	67° 5′	1.32672
0.074	66° 50′	1.32790
0.149	66° 22′	1.32965
0.223	65° 56′	1.33240
0.297	65° 26′	1.33485
0.372	65° 00	1.33684
0.446	64° 35′	1.33894
0.521	64° 10′	1.34106
0.743	63° 00	1.34710

Nickel Nitrate,

$$Ni(NO_3)_2 \text{—} 182.78.$$

Table XIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0761	0.377	4.95
0.1522	0.750	4.93
0.3044	1.527	5.01
0.6088	3.273	5.37
0.7610	4.306	5.66
1.0654	6.691	6.28
1.2176	8.006	6.58
1.5220	10.883	7.15

Table XIV.—Conductivity Measurements.

v.	μ_v.	v.	μ_v.
13.13	90.90	1.31	61.90
6.57	85.14	0.90	55.30
3.25	76.00	0.82	52.28
1.64	68.60	0.65	45.29

Table XV.—Refractivity Measurements.

m.	λ.	n.
0.0761	66° 51'	1.32782
0.1522	66° 25'	1.32989
0.3044	65° 33'	1.33378
0.6088	63° 50'	1.34277
0.7610	63° 05'	1.34667
1.0654	61° 32'	1.35463
1.2176	60° 50'	1.35870
1.5220	59° 24'	1.36653

Nickel Sulphate,

$$NiSO_4 \text{—} 154.76.$$

Table XVI.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.048	0.130	2.70
0.097	0.227	2.34
0.145	0.320	2.21
0.290	0.550	1.90
0.386	0.720	1.87
0.483	0.874	1.81
0.579	1.023	1.77
0.869	1.532	1.76
0.965	1.724	1.79

Table XVII.—Conductivity Measurements.

v.	μ_v.	v.	μ_v.
20.83	54.6	2.07	31.16
10.31	47.1	1.73	29.56
6.89	44.8	1.15	25.08
3.45	37.67	1.03	23.40
2.59	35.92		

Table XVIII.—Refractivity Measurements.

m.	λ.	n.
0.048	67° 00′	1.32711
0.097	66° 40′	1.32869
0.145	66° 25′	1.32989
0.290	65° 30′	1.33436
0.386	64° 55′	1.33726
0.483	64° 25′	1.33978
0.579	63° 45′	1.34320
0.869	62° 25′	1.35018
0.965	61° 55′	1.35285

Nickel chloride shows a minimum in the molecular lowering of the freezing-point in the neighborhood of 0.5 normal. The nitrate of nickel shows the freezing-point minimum at about the same concentration. The sulphate of nickel, like the sulphate of manganese, does not show the freezing-point minimum until a much greater concentration is reached than that at which it appeared with the chloride and nitrate. The positions of the minima in the case of the three salts of nickel can be seen at once by referring to Fig. V. This also shows the actual values of the molecular lowerings produced by the three salts. The chloride gives a molecular lowering of 6.12 at 0.743 normal; the nitrate at this concentration giving a molecular lowering of only about 5.6. The most concentrated solution of the nitrate investigated—1.522 normal—gave, however, a molecular lowering as great as 7.15.

The molecular lowering of nickel sulphate, in addition to showing a minimum, presents another point of very special interest. The molecular lowering produced by nickel sulphate is very small, and in the most concentrated solutions studied is less than the constant for water. This means that in such solutions the nickel sulphate is polymerized, and to

an extent that more than overcomes any electrolytic disso-
ciation that may have taken place. Consequently, the molec-
ular lowering is less than would be produced by a completely
undissociated, non-polymerized substance.

The molecular conductivities of all three of the nickel com-
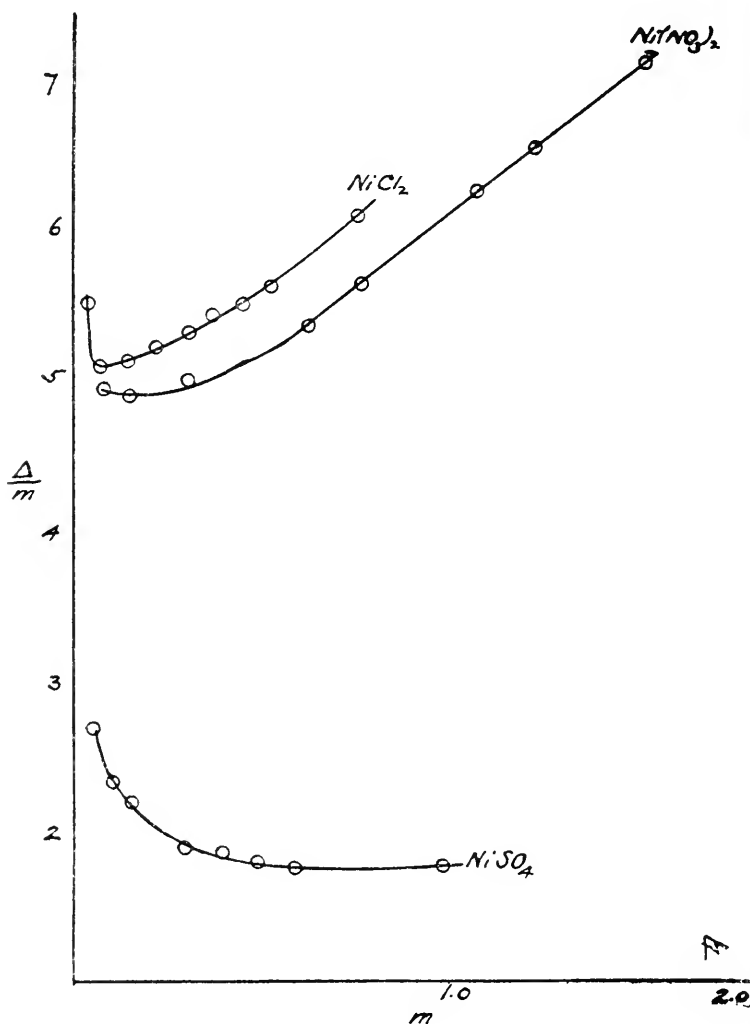
Fig. V.
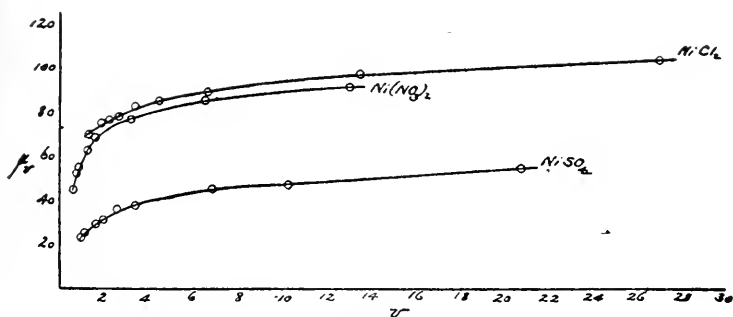
Fig. VI.
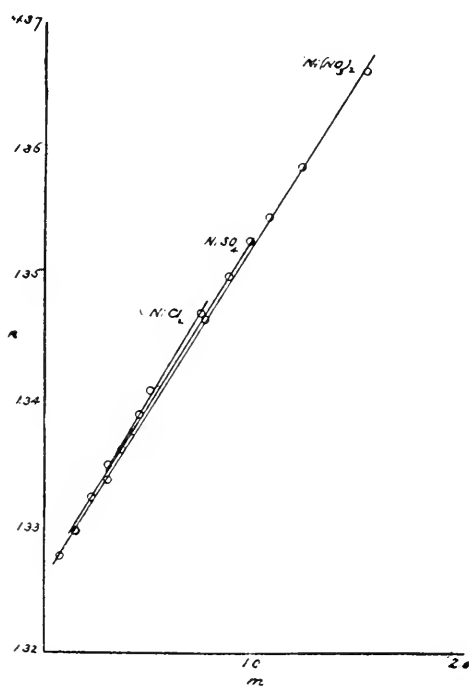
Fig. VII.

pounds increase regularly with the dilution, from the most con-
centrated to the most dilute solution that we employed. This
is seen from the results in tables XI., XIV., and XVII., and
is represented graphically in Fig. VI.

The refractivity data for the three salts of nickel are given in Tables XII, XV., and XVIII. The index of refraction in each case increases regularly with the dilution, and when index of refraction is plotted as one ordinate and concentration as the other, the resulting curve is practically a straight line for all three compounds.

Salts of Cobalt.

The data for the three compounds of cobalt that were studied are given in Tables XIX. to XXVII., and the results are plotted as curves, Figs. VIII. to X.

Cobalt Chloride,

$CoCl_2$—129.9.

Table XIX.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0639	0.325	5.09
0.1279	0.631	4.94
0.1918	0.946	4.93
0.3197	1.640	5.13
0.4475	2.427	5.43
0.5114	2.817	5.51
0.6393	3.658	5.72

Table XX.—Conductivity Measurements.

v.	μ_v.	v.	μ_v.
15.65	95.93	2.23	74.45
7.82	88.42	1.95	71.53
5.21	86.36	1.57	67.94
3.12	79.50		

Table XXI.—Refractivity Measurements.

m.	λ.	n.
0.0639	66° 53′	1.32735
0.1279	63° 27′	1.33005
0.1918	66° 5′	1.33151
0.3197	65° 20′	1.33518
0.4475	64° 37′	1.33910
0.5114	64° 15′	1.34064
0.6393	63° 36′	1.34415

Cobalt Nitrate,

$Co(NO_3)_2 — 183.08.$

Table XXII.—*Freezing-point Measurements.*

m.	Δ.	$\frac{\Delta}{m}$.
0.0747	0.353	4.72
0.1495	0.685	4.58
0.2989	1.388	4.65
0.4484	2.198	4.87
0.7473	3.935	5.28
1.0462	6.025	5.76
1.3451	8.418	6.26
1.4945	9.811	6.55

Table XXIII.—*Conductivity Measurements.*

v.	μ_v	*v.*	μ_v.
13.39	87.68	1.35	62.43
6.69	81.80	0.95	54.60
3.35	75.00	0.74	48.17
2.23	69.46	0.67	45.47

Table XXIV.—*Refractivity Measurements.*

m.	λ.	*n.*
0.0747	66° 50′	1.32790
0.1495	66° 25′	1.32989
0.2989	65° 35′	1.33395
0.4484	64° 48′	1.33837
0.7473	63° 18′	1.34606
1.0462	61° 55′	1.35285
1.3451	60° 30′	1.36053
1.4945	59° 52′	1.36347

Cobalt Sulphate,

$CoSO_4 — 155.06.$

Table XXV.—*Freezing-point Measurements.*

m.	Δ.	$\frac{\Delta}{m}$.
0.0567	0.143	2.52
0.1133	0.245	2.16
0.2267	0.435	1.92
0.3399	0.625	1.84
0.6799	1.187	1.75
0.9066	1.614	1.77
1.1333	2.073	1.82

Table XXVI.—Conductivity Measurements.

v.	μ_v.	v.	μ_v.
17.64	57.49	1.47	30.67
8.82	48.56	1.10	27.16
4.41	42.06	0.89	23.15
2.94	38.07.		

Table XXVII.—Refractivity Measurements.

m.	λ.	n.
0.0567	66° 55′	1.32751
0.1133	66° 35′	1.32909
0.2267	65° 57′	1.33248
0.3399	65° 20′	1.33518
0.6799	63° 37′	1.34423
0.9066	62° 30′	1.34974
1.1199	62° 00′	1.35240
1.1333	61° 30′	1.35508

The chloride of cobalt shows a minimum in the molecular lowering of the freezing-point at a concentration of about 0.2 normal. The nitrate shows the minimum at about the same concentration, while the sulphate does not show a minimum in the molecular lowering of the freezing-point until a concentration of 0.7 to 0.8 normal is reached.

It is also worth noting that the chloride of cobalt, like the chloride of nickel and the chloride of manganese, gives a greater lowering of the freezing-point of water, at the same concentration, than the corresponding nitrate.

The above results are shown graphically in Fig. VIII. The chloride gives a molecular lowering of 5.72 at 0.6393 normal, while the nitrate at this concentration produces a molecular lowering of about 5.0. The most concentrated solution of the nitrate, 1.4948 normal, showed a molecular lowering of 6.55.

The molecular lowering produced by cobalt sulphate, like that of nickel sulphate, is very small indeed. In the most concentrated solutions studied it is less than the constant for water. This is to be interpreted in the same manner as in the case of the nickel salt. There is undoubtedly polymerization here, to such an extent as to more than overcome the effect of electrolytic dissociation.
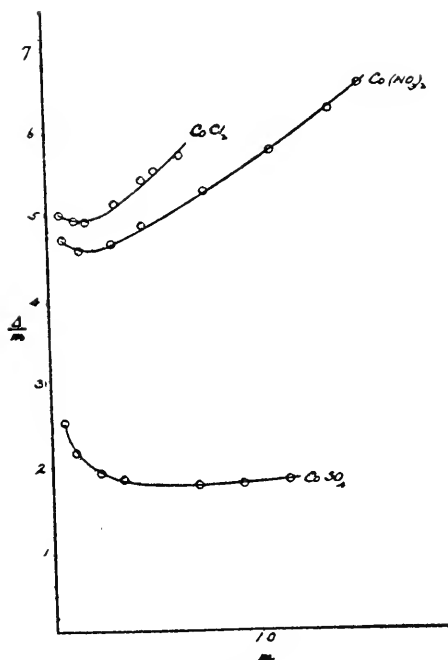
Fig. VIII.
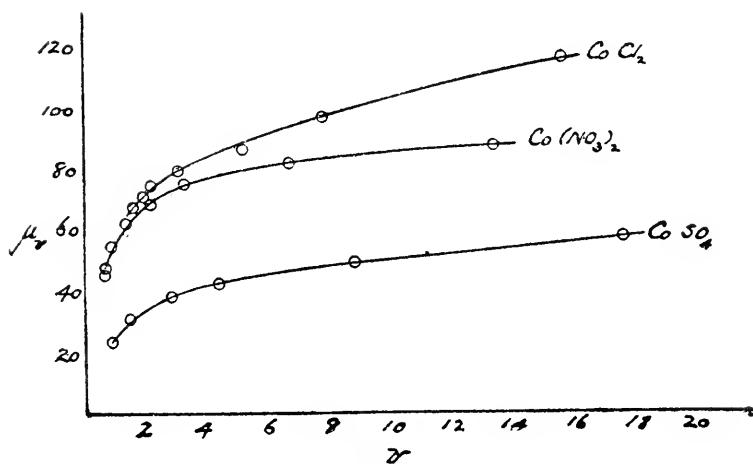
Fig. IX.
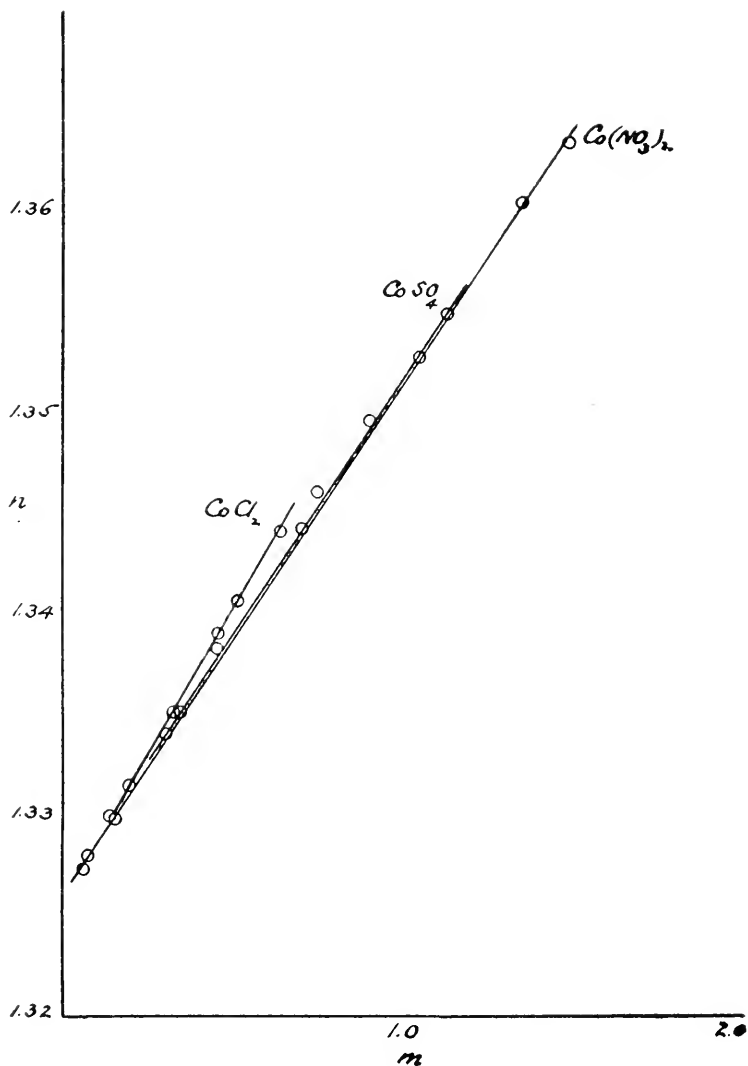
Fig. X.

The conductivities of the three salts of cobalt are given in Tables XX., XXIII., and XXVI., and are plotted in Fig. IX. The curves are all perfectly regular. It should be noted that the conductivity results resemble the freezing-

point results in this, that the chloride has greater conductivity than the nitrate for comparable concentrations, and the nitrate in turn has greater conductivity than the sulphate. This applies also to the salts of nickel and of manganese. The above results are what would be expected, since the chloride and nitrate are ternary electrolytes, while the sulphate is a binary electrolyte.

The refractivities of the three salts of cobalt are given in Tables XXI., XXIV., and XXVII., and plotted against concentration in Fig. X. The curves are perfectly regular and are nearly straight lines.

Copper Salts.

The results obtained with the three salts of copper are given in Tables XXVIII. to XXXIV.

Cupric Chloride,
$$CuCl_2—134.5.$$
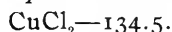
Table XXVIII.—*Freezing-point Measurements.*

m.	Δ.	$\dfrac{\Delta}{m}$.
0.065	0.331	5.09
0.1301	0.639	4.91
0.2602	1.273	4.89
0.5204	2.711	5.29
0.7806	4.413	5.65
1.3010	8.395	6.45
1.5612	10.383	6.65
1.8210	12.960	7.12
2.0816	15.480	7.43
2.6020	20.820	8.00

Table XXIX.—*Conductivity Measurements.*

v.	μ_v.	Dissociation. Per cent.
15.3	94.42	58.5
7.64	88.06	53.4
3.84	78.38	47.5
1.92	67.68	41.0
1.28	59.30	35.9
0.76	48.22	29.2
0.64	39.32	23.8
0.55	35.02	21.2
0.48	30.81	18.9
0.38	22.58	13.7

$$\mu\infty\,0°\,^{[1]} \quad 165$$

[1] For the determination of this and subsequent values of $\mu\infty$ see page 351.

Table XXX.—*Refractivity Measurements.*

m.	λ.	n.
0.065	66° 53′	1.32735
0.1301	66° 25′	1.32989
0.2602	65° 39′	1.33428
0.5204	64° 10′	1.34106
0.7806	62° 45′	1.34842
1.3010	60° 12′	1.36163
1.5612	58° 55′	1.36934
1.8210	57° 43′	1.37579
2.0816	56° 40′	1.38222
2.6020	54° 30′	1.39491

Cupric Nitrate,
$$Cu(NO_3)_2—187.68.$$

Table XXXI.—*Freezing-point Measurements.*

m.	Δ.	$\frac{\Delta}{m}$.
0.0591	0.326	5.52
0.1182	0.595	5.03
0.2363	1.210	5.12
0.4726	2.544	5.39
0.9452	5.903	6.26
1.1815	7.799	6.60
1.6541	12.650	7.07
1.8904	15.490	8.20
2.3630	21.890	9.26

Table XXXII.—*Conductivity Measurements.*

v.	μ_v.	Dissociation. Per cent.
16.9	99.36	64.1
8.46	93.05	60.0
4.23	82.97	52.3
2.12	73.16	47.2
1.05	58.45	37.7
0.84	52.34	33.3
0.60	40.70	26.3
0.52	35.84	23.1
0.42	26.70	17.2

$$\mu_\infty 0° \quad 155$$

Table XXXIII.—Refractivity Measurements.

m.	λ.	n.
0.0591	66° 55′	1.32751
0.1182	66° 30′	1.32949
0.2363	65° 51′	1.33199
0.4726	64° 25′	1.32979
0.9452	61° 50′	1.35329
1.1815	60° 40′	1.35961

Cupric Sulphate,

$CuSO_4$—159.66.

Table XXXIV.

m.	Δ.	$\frac{\Delta}{m}$.
0.072	0.172	2.33
0.144	0.312	2.16
0.476[1]	0.714	1.50
0.595[1]	0.866	1.45
0.890[1]	1.275	1.43
1.190[1]	1.740	1.46

The results are plotted as curves in Figs. XI. to XIII. The minimum in the molecular lowering of the freezing-point occurs, for copper chloride, at about 0.2 normal, for copper nitrate at about 0.1 normal, while for copper sulphate an apparent minimum occurs at about 0.9 normal, but this is not well defined.

There are a number of points of interest in connection with the freezing-point data and curves (Fig. XI.) of the copper salts. In the first place one is impressed with the great magnitude of the molecular lowering in concentrated solution, of copper chloride and copper nitrate. The chloride, at a concentration of 2.6 normal, shows a molecular lowering of 8.0 ; while the nitrate, at a concentration of 2.363 normal, gives a molecular lowering of 9.26. This is the largest molecular lowering produced by any substance thus far recorded in this paper. It might, also, be noted that copper nitrate gives a larger lowering, for comparable concentration, than copper chloride, which is the opposite of what was observed with manganese, nickel, and cobalt.

The molecular lowering of the freezing-point of water pro-

[1] Measurements by Chambers and Frazer. This JOURNAL, **23**, 512.

duced by copper sulphate is smaller than that produced by any other compound which has come within the scope of our work. It falls to 1.43 at a concentration of 0.89 normal, and then apparently increases slightly with increase in concentration. Since this value is so far below the constant for water, 1.86, we must conclude that there is considerable polymerization in the more concentrated solutions of copper sulphate.

The conductivities of copper chloride and copper nitrate (Tables XXIX. and XXXII., and Fig. XII.) increase regularly with the dilution.

The conductivity of copper nitrate, like the freezing-point lowering is, for comparable concentrations, greater than that
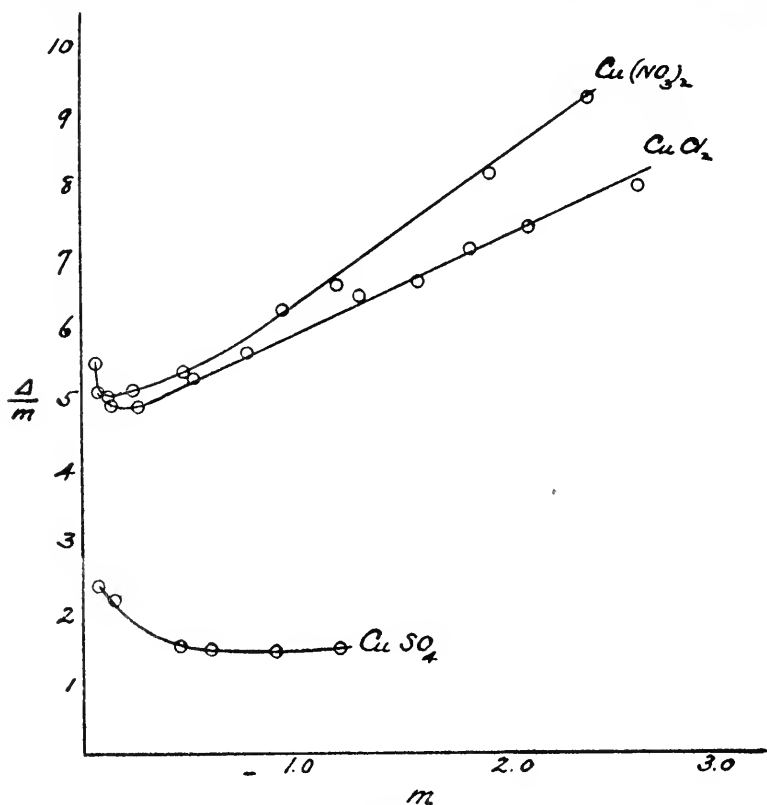
Fig. XI.
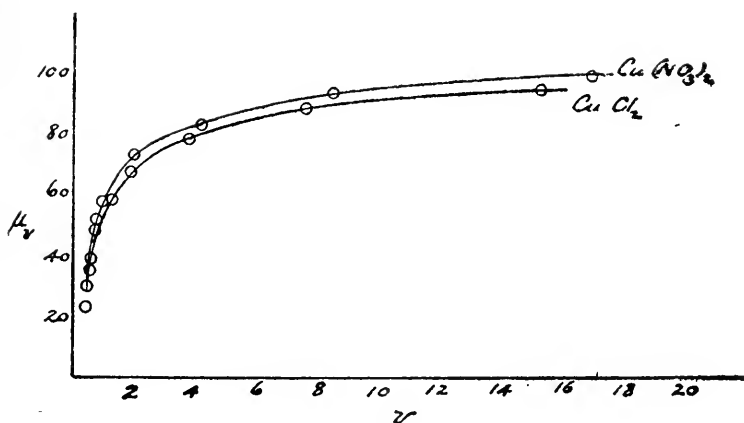
Fig. XII.
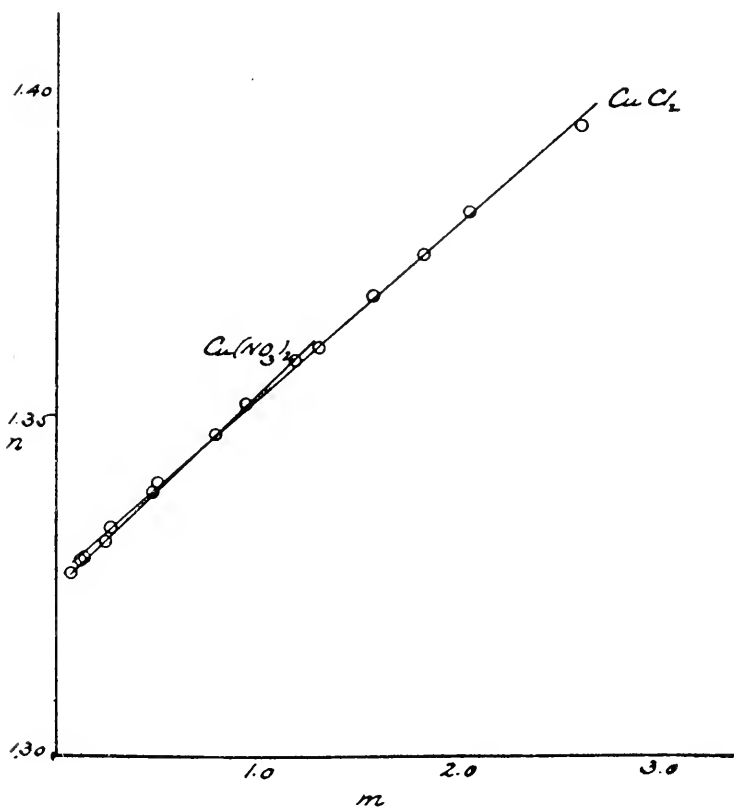
Fig. XIII.

of the chloride. The opposite was observed with the chlorides and nitrates of manganese, nickel, and cobalt. Since it was impossible to prepare a very concentrated solution of copper sulphate, the conductivities of this substance were not measured.

The refractivities of cupric chloride and nitrate are given in Tables XXX. and XXXIII., and the results are plotted in Fig. XIII. The refractivities of copper sulphate were not measured, since concentrated solutions could not be prepared. The refractivity curves of the chloride and nitrate are practically straight lines, showing no irregularity.

Salts of Aluminium.

The results for the three salts of aluminium are given in Tables XXXV. to XLVI. They are plotted in curves, Figs. XIV. to XVI. The minimum in the molecular lowering for aluminium chloride is at about 0.1 normal, and at about the same concentration for aluminium nitrate. No minimum was observed in the case of aluminium sulphate, probably because a solution of sufficient concentration could not be prepared.

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Aluminium Chloride,

$AlCl_3$—133.46.
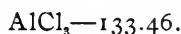
Table XXXV.—Freezing-point Measurements.

</div>

m.	Δ.	$\frac{\Delta}{m}$.
0.046	0.276	6.04
0.076	0.446	5.85
0.102	0.578	5.68
0.200	1.148	5.74
0.299	1.840	6.15
0.398	2.596	6.52
0.531	3.830	7.21
0.657	5.120	7.79
0.876	7.970	9.09
1.195	13.610	11.40
1.434	19.518	13.60
1.593	23.870	14.98
2.124[1]	45.000	21.18

[1] This solution was frozen by means of a mixture of solid carbon dioxide and alcohol, and the freezing temperature measured by an alcohol thermometer.

Table XXXVI.—Conductivity Measurements.

v.	μ_v.	Dissociation. Per cent.
18.80	124.6	73.3
4.70	104.6	59.8
2.35	88.64	52.1
1.45	71.7	42.2
0.94	59.3	34.9
0.67	43.1	25.3

$$\mu\infty\,0° = 170$$

Table XXXVII.—Refractivity Measurements.

m.	λ.	n.
0.2124	$65°\ 43'$	1.33297
0.4248	$64°\ 15'$	1.34064
0.6372	$62°\ 53'$	1.34736
1.062	$60°\ 20'$	1.36145
1.0487	$57°\ 54'$	1.37493
2.124	$54°\ 35'$	1.39441

Table XXXVIII.—Specific Gravity Measurements.

m.	W_S.	W_{AlCl_3}.	W_{H_2O}.	Correction. Per cent.
0.2124	25.5593	0.7087	24.8506	0.60
0.4248	26.1216	1.4173	24.7043	1.18
0.6372	26.6408	2.1260	24.5142	1.94
1.0620	27.6952	3.5430	24.1522	3.39
1.4868	25.6581	4.9600	23.6981	5.21
2.1240	30.0789	7.0870	22.9190	8.32

Aluminium Nitrate,
$$Al(NO_3)_3—213.23.$$
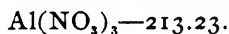
Table XXXIX.—Freezing-point Measurements.

m.	Δ.	$\dfrac{\Delta}{m}$.
0.0533	0.333	6.25
0.1066	0.652	6.12
0.2132	1.410	6.57
0.3198	2.290	7.15
0.5330	4.260	8.00
0.7462	6.760	9.06
0.8528	8.190	9.60
1.066	11.790	11.06

Table XL.—*Conductivity Measurements.*

$v.$	$\mu_v.$	Dissociation. Per cent.
18.76	137.85	76.6
9.38	122.00	67.8
4.69	111.89	62.1
3.13	101.60	56.4
1.88	86.10	47.8
1.34	73.27	40.7
1.17	65.98	36.6
0.94	55.21	30.6

$$\mu\infty\ 0° = 180$$

Table XLI.—*Refractivity Measurements.*

$m.$	$\lambda.$	$n.$
0.0533	$66°\ 52'$	1.32727
0.1066	$66°\ 30'$	1.32949
0.2132	$65°\ 40'$	1.33354
0.3198	$64°\ 54'$	1.33726
0.5330	$63°\ 25'$	1.34493
0.7462	$62°\ 00'$	1.35240
0.8528	$61°\ 10'$	1.35688
1.066	$60°\ 5'$	1.36283

Table XLII.—*Specific Gravity Measurements.*

$m.$	$W_S.$	$W_{Al(NO_3)_3}.$	$W_{H_2O}.$	Correction. Per cent.
0.0533	25.1615	0.2840	24.8775	0.49
0.1066	25.3858	0.5682	24.8176	0.73
0.2132	25.8260	1.1362	24.6898	1.24
0.3198	26.2487	1.7045	24.5442	1.82
0.5330	27.1053	2.8400	24.2653	2.94
0.7462	27.9300	3.9760	23.9540	4.18
0.8528	28.3283	4.5460	23.7823	4.87
1.0660	29.1080	5.6820	23.4260	6.30

Aluminium Sulphate,
$$Al_2(SO_4)_3 — 342.43.$$
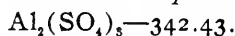
Table XLIII.—*Freezing-point Measurements.*

$m.$	$\Delta.$	$\frac{\Delta}{m}.$
0.0736	0.260	3.46
0.1841	0.683	3.71
0.2946	1.138	3.86
0.3682	1.521	4.13

Table XLIV.—Conductivity Measurements.

$v.$	$\mu_v.$
13.58	80.62
5.43	62.41
3.39	50.84
2.71	44.89

Table XLV.—Refractivity Measurements.

$m.$	$\lambda.$	$n.$
0.0736	$66°\ 13'$	1.33086
0.1841	$64°\ 40'$	1.33852
0.2946	$63°\ 16'$	1.34588
0.3682	$62°\ 25'$	1.35018

Table XLVI.—Specific Gravity Measurements.

$m.$	$W_S.$	$W_{Al_2(SO_4)_3}.$	$W_{H_2O}.$	Correction. Per cent.
0.0736	25.5612	0.6300	24.9312	0.28
0.1841	26.4130	1.5757	24.8373	0.65
0 2946	27.3215	2.5200	24.8015	0.79
0.3682	27.9238	3.1500	24.7738	0.90

In examining the freezing-point data for aluminium chloride and nitrate, one is especially impressed with the enormous magnitude of the molecular lowering produced by these substances, aluminium chloride showing an apparent molecular lowering of 21.18 at 2.124 normal. Aluminium nitrate shows even a greater molecular lowering than the chloride for the concentrations at which it could be studied, as can be seen at once from the continuous curves in Fig. XIV. The molecular lowering shown by the most concentrated solution of aluminium chloride is nearly double that found for any other substance which we have studied. The significance of these facts will be taken up in the general discussion of the results. The large lowerings shown by aluminium chloride and nitrate in dilute solutions are doubtless due, in part, to hydrolysis.

The molecular conductivities of the aluminium compounds increase regularly with the dilution, as can be seen in Tables XXXVI., XL., and XLIV., and in Fig. XV. The nitrate has greater conductivity than the chloride, which is analogous to the freezing-point results.

The refractivities of the three compounds of aluminium
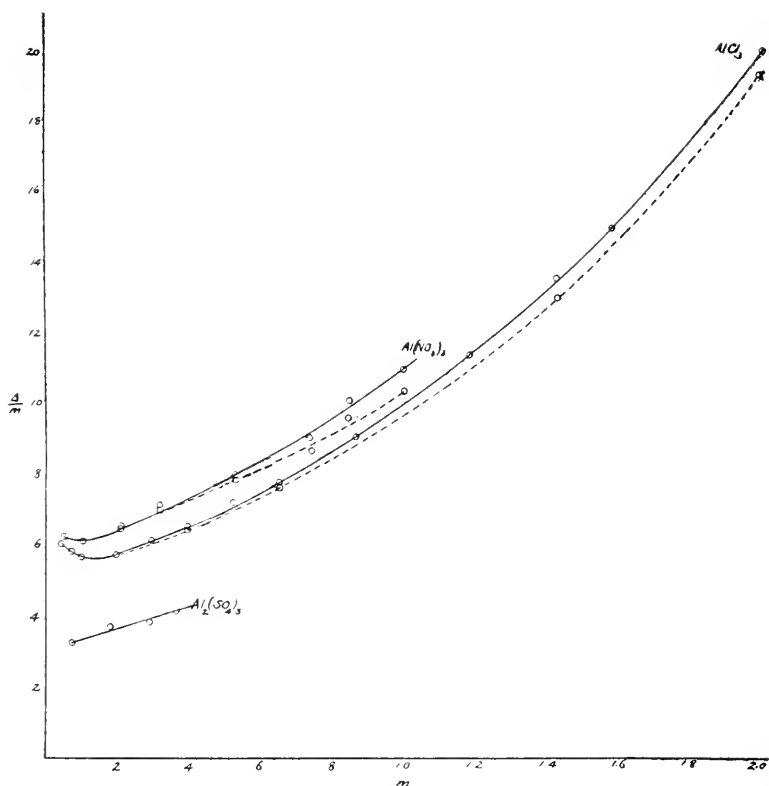
Fig. XIV.
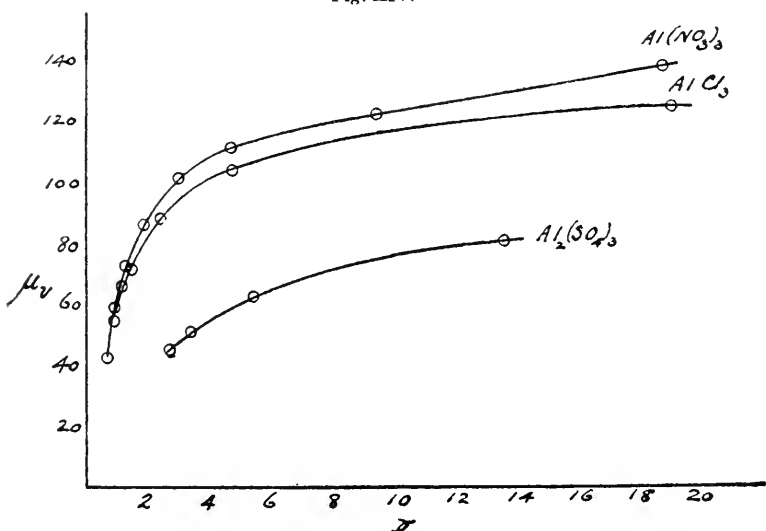
Fig. XV.
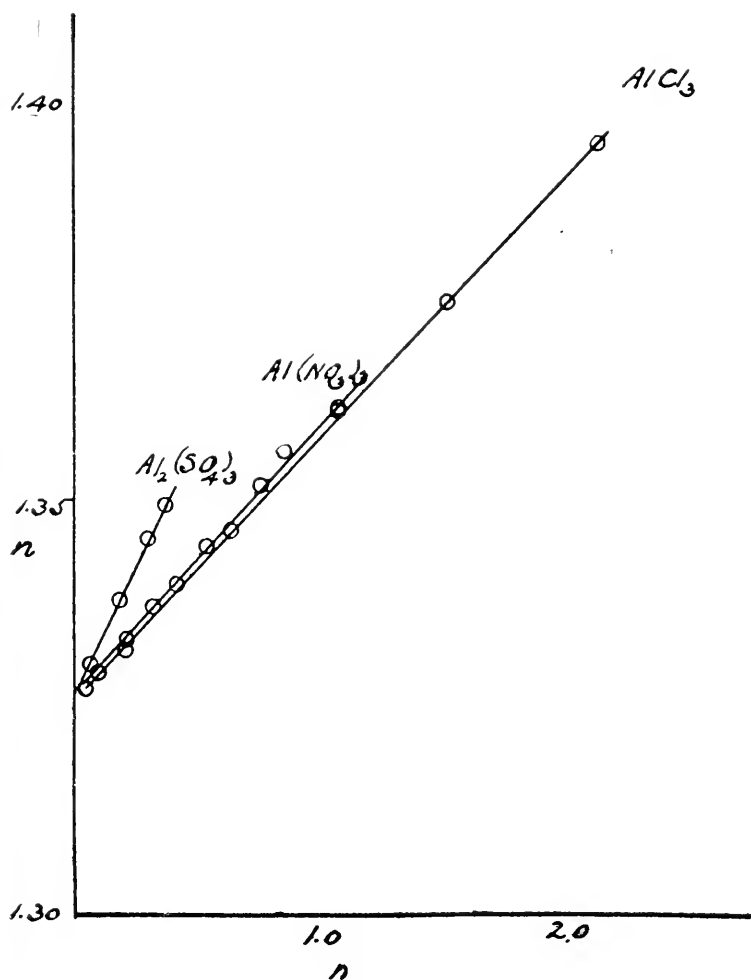
Fig. XVI.

(Table XXXVII., XLI., XLIV., and Fig. XVI.) are per-
fectly regular, always increasing with the concentration.

Specific gravity measurements were made and recorded
with the three salts of aluminium. m is the concentration of
the solution in terms of gram-molecular weight of the salt in
a liter of the solution; W_s is the weight of 25 cc. of solution;

W_{AlCl_3} is the weight of aluminium chloride in 25 cc. of the
the solution; W_{H_2O} is the weight of water in 25 cc. of the
solution, and "Correction" is the percentage difference be-
tween the weight of water in 1 liter of the solution and
1,000 grams of water. In the more concentrated solutions
this correction term becomes quite large — the amount of
water in a liter of such solutions being much less than 1,000
grams.

In order that we should be able to calculate the amount of
water combined with 1 molecule of the salt, as will be done
later in this paper, this correction must be applied to the ap-
parent molecular lowerings, giving the true molecular lower-
ings, which are the quantities that are nearly comparable
with one another at all concentrations, and which can be com-
pared directly with the freezing-point constant of water—1.86.

These corrections have already been applied to aluminium
chloride and nitrate, and will be applied in a later paper
to many other substances already studied, and to those
that we are about to take up. The corrected results for the
two compounds of aluminium are shown in the dotted curves,
Fig. XIV. These are the true molecular lowerings produced
by these substances, referred in every case to 1,000 grams of
the solvent. The difference between the true and the ob-
served lowerings becomes greater, of course, as the concentra-
tion increases. Reference will be made again to these results
under the general discussion.

Determination of Rise in Boiling-points.

The rise in the boiling-point of water produced by a few
compounds has been measured, using the Jones[1] apparatus,
and the results are recorded in Tables XLVII. to LI.

In all of these determinations two pieces of apparatus were
used, the one containing the pure solvent and the other the solu-
tion. They were both kept boiling simultaneously, and thus
correction for barometric changes was avoided.

We have not yet had time to extend these measurements
to a large number of substances. Although the task seems
to be somewhat difficult, we hope to apply the boiling-point

[1] This JOURNAL, **19**, 581 (1897).

Potassium Iodide (166.0) in Ethyl Alcohol.

Table XLVII.—Boiling-point Measurements.

First Series.

m.	f.	$\frac{f}{m}$.
0.052	0.080	1.54
0.061	0.090	1.47
0.073	0.106	1.45
0.088	0.125	1.42
0.125	0.175	1.40
0.174	0.250	1.43
0.237	0.343	1.45
0.250	0.355	1.42
0.266	0.373	1.40
0.286	0.407	1.42
0.296	0.420	1.42
0.317	0.450	1.42
0.337	0.479	1.42

Second Series.

0.045	0.070	1.55
0.060	0.090	1.50
0.071	0.105	1.48
0.095	0.140	1.47
0.102	0.150	1.47
0.112	0.165	1.47
0.145	0.213	1.47
0.373	0.530	1.42

Third Series.

0.021	0.032	1.54
0.032	0.050	1.56
0.045	0.070	1.55

Sodium Iodide (149.9) in Ethyl Alcohol.

Table XLVIII.

First Series.

m.	f.	$\frac{f}{m}$.
0.031	0.060	1.94
0.063	0.120	1.91
0.108	0.185	1.71
0.179	0.290	1.62
0.227	0.370	1.62
0.306	0.500	1.63
0.415	0.669	1.61
0.461	0.730	1.58

Second Series.

m.	f.	$\frac{f}{m}$.
0.042	0.080	1.90
0.092	0.150	1.74
0.123	0.205	1.67
0.139	0.225	1.62
0.601	0.925	1.54
0.875	1.440	1.64
1.344	2.470	1.83
1.661	3.300	1.99

Third Series.

0.022	0.045	2.05
0.041	0.078	1.90
0.076	0.125	1.64
0.140	0.225	1.61
0.230	0.360	1.56
0.307	0.480	1.56

Cadmium Iodide (366.1) in Ethyl Alcohol.

Table XLIX.

First Series.

m.	f.	$\frac{f}{m}$.
0.069	0.080	1.16
0.122	0.142	1.16
0.190	0.225	1.18
0.243	0.305	1.26
0.327	0.420	1.28
0.478	0.610	1.28
0.786	1.060	1.34
0.822	1.150	1.40
1.174	1.600	1.36
1.340	1.860	1.39
1.488	2.100	1.41
1.674	2.360	1.41
1.829	2.580	1.41

Second Series.

0.042	0.052	1.24
0.135	0.162	1.20
0.169	0.207	1.22
0.220	0.272	1.24
0.252	0.316	1.25
0.312	0.392	1.26
0.471	0.597	1.27
0.529	0.680	1.29

Third Series.

m.	f.	$\frac{f}{m}$.
0.012	0.018	1.50
0.041	0.050	1.22
0.058	0.068	1.17
0.089	0.110	1.23
0.119	0.142	1.19
0.156	0.188	1.21

Ammonium Iodide (144.94) in Ethyl Alcohol.

Table L.

First Series.

m.	f.	$\frac{f}{m}$.
0.017	0.030	1.76
0.056	0.090	1.60
0.134	0.200	1.49
0.178	0.265	1.49
0.231	0.350	1.52
0.277	0.435	1.57

Second Series.

0.019	0.032	1.68
0.031	0.051	1.64
0.077	0.120	1.56
0.124	0.190	1.53
0.150	0.222	1.47
0.185	0.277	1.50

Sodium Bromide (103.0) in Ethyl Alcohol.

Table LI.

First Series.

m.	f.	$\frac{f}{m}$.
0.103	0.140	1.36
0.135	0.185	1.36
0.156	0.210	1.34
0.224	0.290	1.29
0.267	0.335	1.25
0.331	0.395	1.19
0.363	0.440	1.21

Second Series.

m.	f.	$\frac{f}{m}$.
0.014	0.025	1.78
0.030	0.050	1.67
0.054	0.080	1.48
0.065	0.095	1.46
0.098	0.137	1.40
0.136	0.185	1.36
0.237	0.305	1.28
0.318	0.391	1.23

Third Series.

0.019	0.033	1.74
0.055	0.081	1.47
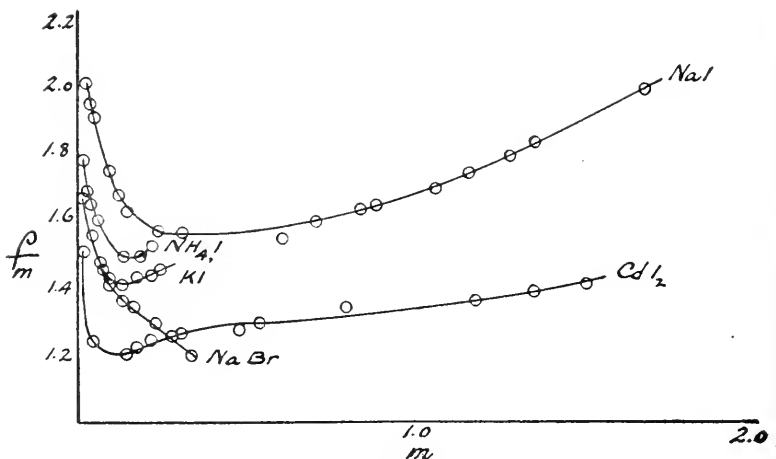
Fig. XVII.

method to a much larger number of the compounds, which have yielded such interesting results when the freezing-point method was applied to them.

Four of the five compounds studied by the boiling-point method show a well-defined minimum in the molecular rise of the boiling-point. Sodium bromide does not show such a minimum. The minimum in the case of rise in boiling-point is generally at a greater concentration than the freezing-point minimum for the same substances. This is exactly what

would be expected if the theory of hydrates in concentrated solutions, to account for these minima and the great freezing-point lowerings in concentrated solutions, is true. *These hydrates would be less stable at the higher temperatures*, and a greater concentration would, therefore, have to be reached before the effect of hydrate formation would so far overcome the influence of electrolytic dissociation as to cause the curve to pass through a minimum. This will, however, be referred to again.

General Discussion of the Results.

We have already studied in this laboratory from the above standpoint forty-nine compounds. Jones and Chambers[1] worked with ten salts. Chambers and Frazer[2] studied five salts and two acids. In our first paper[3] we described our work with twenty-three compounds, including seventeen salts, four acids, and two bases. Six of these substances, however, were the same as those used by Jones and Chambers, and Chambers and Frazer—more concentrated solutions being studied with the thermometers of wider range. In this paper we have given the results obtained for fifteen salts.

Of these forty-nine compounds forty-three are salts, four are acids, and two are bases. All of these substances show a minimum in the molecular lowering of the freezing-point except the following : Jones and Chambers found two exceptions, cadmium chloride and bromide. Chambers and Frazer failed to find more than one exception. Of these substances discussed in our first paper only sodium, potassium, and ammonium nitrates, sodium, potassium, and ammonium sulphates, and primary potassium phosphate failed to show a minimum in the freezing-point curve. Of the fifteen substances discussed in this paper, only aluminium sulphate fails to show any sign of a minimum, and, as is seen from the curve, Fig. XIV., this is because the proper dilution was not used. The minimum in the cases of nickel and cobalt sulphates is not very pronounced, but undoubtedly exists.

[1] This JOURNAL, **23,** 89 (1900).

[2] *Ibid.*, **23,** 512 (1900).

[3] Ztschr. phys. Chem., **46,** 244 (1903). Phys. Rev., **18,** 146 (1904).

Of the forty-nine compounds that have been studied in this laboratory only nine failed to show a minimum in the freezing-point curve. Some of these nine substances, however, showed abnormally great freezing-point lowerings in concentrated solutions, the normal freezing-point lowering of each being calculated from the conductivity.

Nearly every one of the forty-nine substances which we have studied, whether it does or does not show a freezing-point minimum, gives abnormally great depressions of the freezing-point of water in concentrated solutions, except two or three sulphates which are obviously polymerized in such solutions since the molecular lowerings are less than the constant for water. Some compounds show this phenomenon to a much greater extent than others, but they show it.

Explanation of the Above Fact.

The suggestion was made by Jones and Chambers[1] four years ago, to account for their results, that possibly the compounds, such as they had studied, combined with water in the more concentrated solutions. This suggestion was put forward purely tentatively, since it was the only apparent explanation of their results. They pointed out, however, as evidence in favor of this suggestion, that the chlorides and bromides of the alkaline earths, the substances with which they worked, were generally very hygroscopic substances when dehydrated, combining readily with water. With this idea in mind, Chambers and Frazer,[2] at the suggestion of Jones, with whom their work was done, selected those substances that are particularly hygroscopic, and found in every case, with the exception of copper sulphate, that the lowering in concentrated solutions was abnormally great.

Relation Between Water of Crystallization and Freezing-point Lowering.

We then took up the subject from a broader standpoint, determining to study all classes of substances with respect to this property. We find that while all substances except cer-

[1] This JOURNAL, **23**, 89 (1900).
[2] *Ibid.*, **23**, 512 (1900).

tain polymerized sulphates ($CuSO_4$, $NiSO_4$, $CoSO_4$) give abnormally great lowerings in concentrated solutions, the magnitude of this lowering varies greatly from one substance to another, and in general *those substances which crystallize out of solution with the largest number of molecules of water of crystallization, give the greatest molecular lowerings of the freezing-point of water in concentrated solution.* To take examples from our first paper, of all the chlorides studied in this part of our work, only calcium and strontium chlorides crystallize with six molecules of water. Barium chloride crystallizes with two molecules. Lithium chloride crystallizes below zero with two molecules of water of crystallization, while the alkali chlorides separate from solution with no water of crystallization. An examination of Fig. III., in our earlier paper,[1] will show that the curve for lithium chloride falls between those for the alkalies and the alkaline earths, and that the lowerings produced by calcium and strontium chlorides are very much greater than those produced by the alkali chlorides.

If we include also the work of Jones and Chambers,[2] which, however, did not extend to any very great concentration, we find that magnesium chloride, which, like calcium and strontium chlorides, has 6 molecules of water of crystallization, gives freezing-point depressions of the same order of magnitude as calcium and strontium chlorides; indeed, slightly larger depressions. Cadmium chloride, on the other hand, crystallizes with only 2 molecules of water and shows much less depression of the freezing-point.

The work of Jones and Chambers[3] shows that exactly the same relations obtain for the bromides of barium, strontium, calcium, and magnesium, as we have just seen to hold for the chlorides. Barium bromide crystallizes with 2 molecules of water, and gives the smallest lowering; strontium, calcium, and magnesium bromides each crystallize with 6 molecules of water of crystallization, and stand in the same order with re-

[1] Ztschr. phys. Chem., **46**, 281 (1903). Phys. Rev., **18**, 146, (1904).
[2] This JOURNAL, **23**, 96 (1900).
[3] *Loc. cit.*

spect to freezing-point lowerings as the corresponding chlorides.

When we turn to our results[1] for the nitrates of potassium, ammonium, sodium, and lithium, exactly the same relations appear. The first three have no water of crystallization, and give freezing-point lowerings of the same order of magnitude. Lithium nitrate crystallizes with 2.5 molecules of water, and gives much greater lowering than the three alkali nitrates in question.

In our earlier work we studied the sulphates[2] of sodium, potassium, and ammonium. Two of these have no water of crystallization, and the third, sodium sulphate, separates with varying amounts of water, or with none, depending upon the temperature.

The carbonates[3] of sodium and potassium were also studied in the first work that we did, and present an apparent exception to the above relation ; sodium carbonate crystallizes with more water than potassium carbonate, yet shows a smaller lowering of the freezing-point. Sodium carbonate is however, strongly efflorescent, showing that it holds the ten molecules of water in unstable combination.

Turning to the work recorded in this paper, the number of exceptions is somewhat larger, although nearly all of the fifteen compounds crystallize with a large amount of water, as can be seen from the following table :

Table LII.

$MnCl_2.4H_2O$	$NiCl_2.6H_2O$	$CoCl_2.6H_2O$
$Mn(NO_3)_2.6H_2O$	$Ni(NO_3)_2.6H_2O$	$Co(NO_3)_2.6H_2O$
$MnSO_4.7H_2O$	$NiSO_4.7H_2O$	$CoSO_4.7H_2O$
$CuCl_2.2H_2O$	$AlCl_3.6H_2O$	
$Cu(NO_3)_2.3H_2O$	$Al(NO_3)_3.8H_2O$	
$CuSO_4.5H_2O$	$Al_2(SO_4)_3.9H_2O$	

The sulphates all show much less lowering of the freezing-point than the corresponding chlorides and nitrates, notwithstanding the fact that they crystallize with more water than

[1] Ztschr. phys. Chem., **46**, 281 (1903), Fig. IV.   Phys. Rev., **18**, 146 (1904).

[2] *Ibid.*, Fig. V.

[3] *Ibid.*, Fig. VI.

either of the other corresponding compounds. It must, however, be remembered that the sulphates in question are all binary electrolytes, while the chlorides and nitrates are ternary electrolytes, and, further, what is more important, the sulphates undoubtedly undergo polymerization in concentrated solutions, shown by the fact that such compounds as nickel sulphate, cobalt sulphate, and copper sulphate give, in such solutions, molecular lowerings that are much less than the constant for water. It is, therefore, impossible to say with how many molecules of water such sulphates are combined in solution, since we have these two influences—polymerization and possible hydration acting counter to one another at the same time, and no means of determining the magnitude of either in the presence of the other.

When we turn to the chlorides the only apparent exception is presented by cupric chloride, which is not closely allied chemically to the other chlorides. Manganese chloride with four molecules of water of crystallization gives less lowering than nickel and cobalt chlorides, each with six molecules of water of crystallization, the last two giving just about the same lowering. Aluminium chloride gives a much greater lowering than either nickel or cobalt chloride, although it contains the same number of molecules of water of crystallization. This would, however, be expected since aluminium chloride is a quarternary electrolyte, while the other two are binary electrolytes. The only apparent departure from our generalization in connection with these five chlorides is cupric chloride. It crystallizes with only two molecules of water, and yet gives about the same lowering, for comparable concentrations as nickel and cobalt chloride. Since cupric chloride differs so widely chemically from the other chlorides, it really should not be compared with them, and is, then, not a true exception. When we turn to the nitrates of the five elements studied in this part of our investigation, the relations are as satisfactory as those just discussed for the chlorides. Manganese nitrate, however, gives considerably less lowering than nickel and cobalt nitrates, although it contains the same number of molecules of water of crystallization. Nicke

nitrate and cobalt nitrate give about the same lowering, and have the same number of molecules of water of crystallization. Aluminium nitrate gives greater lowering than any other compound thus far studied. It crystallizes with eight molecules of water. At the great concentration employed it should be stated that hydrolysis has very little effect on our results, even in the case of the aluminium compounds.

Copper nitrate presents the only apparent exception among the five nitrates. It gives about the same lowering as the nitrates of nickel and cobalt, but crystallizes with only half as much water. For the reasons given above for copper chloride, it should not be brought into this comparison. It is then made evident from the above discussion that there is a *relation between the freezing-point lowering in concentrated solutions and the water of crystallization of the compound*. The number of cases that conform to this relation is so large, and the number of exceptions so small, that the agreement cannot be regarded as accidental.

This relation is strong evidence in favor of our theory that the *very great freezing-point lowerings in concentrated solutions is to be explained by the existence of hydrates in such solutions*. Other things being equal, those substances that crystallize from solution with the largest amounts of water, would be the ones that would combine with the largest amounts of water in solution. The amount of water with which a molecule of any substance can combine in a concentrated solution may, however, be much greater than that which it can carry with it from the solution in a stable form ; may be much greater than its water of crystallization.

We have also seen that a large number of substances, indeed, practically all of the forty-nine compounds investigated, give lowerings of the freezing-point in concentrated solutions that are larger than those that would be calculated from their dissociation. Many of these compounds crystallize from such solutions without any water of crystallization. Our theory of the existence of hydrates in concentrated solutions applies as well to these as to other substances. These substances, as we have seen, do not show a molecular lowering as large as

those substances that have water of crystallization. This means that such substances do not combine in solution with as many molecules of water as those with water of crystallization. We would, therefore, not expect them to be able to hold, in a stable condition, as many molecules of water of crystallization outside of solution, as those substances which combine with a larger number of water molecules in solution, and such is the fact. Indeed, where they are combined with very few molecules of water in solution, as is shown by the freezing-point lowerings to be the case with a number of the compounds already studied, we would expect such compounds to separate from solution without any water of crystallization, and such is the fact.

Not a single one of the forty-nine compounds studied, which crystallizes from solution without water of crystallization shows very great lowering in concentrated solution. A better agreement between fact and theory could scarcely be asked.

It should, however, not be forgotten that while, in concentrated solutions of apparently almost all electrolytes, we have hydrates of greater or less complexity, we have also some of the molecules broken down into ions. This is shown by the fact that such solutions always conduct the electric current to a greater or less extent. The conductivity curves are, as we have seen, in all cases regular, with no sign of any minimum, showing that the dissociation proceeds regularly as we increase the dilution of the solution. The same observation applies to the refractivity curves. They are always perfectly regular from the most concentrated to the most dilute solution investigated.

Let us now see exactly what the minima in the freezing-point curves mean. Starting with the most dilute solution, the curves gradually fall with increase in concentration, due to the diminution of dissociation. Finally, a concentration is reached where the hydrates with a few molecules of water begin to form. These diminish the amount of water acting as solvent by just so much, and tend to increase the molecular lowering of the freezing-point. Finally, at a definite concentration for each substance, these two opposite influences are
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equal and we have the minimum in the curve. As the concentration becomes still greater more complex hydrates form, and this effect far overcomes the opposite effect due to diminishing dissociation, and the freezing-point curves rise. This influence becomes greater and greater, the greater the concentration, and the opposite influence, due to diminishing dissociation, becomes less and less, and the freezing-point curve continues to rise with the concentration, at least as far as the most concentrated solutions that we have studied.

Our theory thus accounts, in a most satisfactory manner, for the facts.

Calculation of the Composition of the Hydrates.

In order to calculate the exact composition of any hydrate in solution we must know, in addition to the facts recorded in this paper, the exact dissociation of a solution and its specific gravity. We must know the dissociation in order to determine the molecular lowering that would be produced if there was no hydration. We must know the specific gravity to determine the difference between the amount of water in a liter of the solution, and 1,000 grams of water, since molecular lowerings are all referred to 1,000 grams of water, and this difference is very considerable in solutions of such great concentration as some of those which we have used.

We have not had time as yet to obtain such data in many cases, but shall do so as soon as possible. It is not difficult to find good specific gravity measurements recorded for many substances, but these should be determined as near to 0° as possible, and the dissociation must be measured at zero.

We have already obtained the necessary data for cupric chloride and nitrate, and aluminium chloride and nitrate, and have calculated the composition of the hydrates formed by these substances at the various dilutions studied. The specific gravity data in the case of the aluminium salts are given in Tables XXXVIII., XLII., and XLVI., and the dissociations α are taken from Tables XXXVI. and XL. The specific gravity data for the copper salts are taken from the work of others, while the dissociations α (Tables XXIX. and

XXXII.) are calculated from our own conductivity measurements. In calculating the dissociations from conductivity it is necessary to know $\mu\infty$ at the same temperature that the values of μ_v were determined. This we have not yet had time to determine directly in the case of any substance studied in this or the preceding paper. We found that it would be impossible to determine this value directly in such cases as aluminium chloride and nitrate, on account of the great amount of hydrolysis that occurs in dilute solutions of such substances. We have, however, determined $\mu\infty$ for copper chloride and nitrate, and aluminium chloride and nitrate, indirectly, as follows :

From the freezing-point lowering of a dilute solution, α was calculated, knowing α and μ_v for a dilute solution, $\mu\infty$ was calculated at once ; $\mu_v = \alpha\mu\infty$. This calculation was made for each substance, using three dilutions, and the values of $\mu\infty$ for the different dilutions in every case agreed to within a very few units. In the above calculation of $\mu\infty$ we were careful to select only those solutions that were of considerably greater dilution than that at which the minimum in the freezing-point curve manifested itself. In solutions near the freezing-point minimum there would probably still be a little hydration, and the value of α for such solutions, as calculated from freezing-point measurements, would contain some error.

Given the value of $\mu\infty$ for the salt at $0°$, the dissociation at this temperature was calculated from our conductivity measurements in the usual way, $\alpha = \dfrac{\mu_v}{\mu\infty}$.

The dissociations at $0°$ cannot differ appreciably from the dissociations at the freezing-points of the various solutions, since Jones and Douglas[1] showed that the temperature coefficient of dissociation is practically 0, from $0°$ to $25°$.

Given the above data, the calculation of the number of molecules of water combined with 1 molecule of the salt at any dilution is very simple, as would be gathered from an earlier part of this paper. In the first place, the " Observed

[1] This JOURNAL, **26**, 428 (1901).

molecular lowering'' was corrected for specific gravity, giving the '' True molecular lowering.'' The molecular lowering that would be produced if there was no hydration was then calculated from the equation :

$$\frac{\text{Molecular lowering}}{1.86} = i;$$

$$\frac{i - 1}{2} = \alpha \text{ for ternary electrolytes, } (CuCl_2, Cu(NO_3)_2) ;$$

$$\frac{i - 1}{3} = \alpha \text{ for quaternary electrolytes, } (AlCl_3, Al(NO_3)_3).$$

The ratio of the molecular lowering calculated, to the molecular lowering found, multiplied by 1,000, gave the amount of water that was present in 1,000 cc. of the solution as water playing the rôle of solvent. The difference between this amount of water and 1,000 grams was the amount that had combined with 1 gram-molecular weight of the salt, under the conditions present in the solution in question.

Knowing the amount of water in grams that had entered into combination, we determined the number of gram-molecular weights of water by dividing by 18, and this gives us at once the number of molecules of water combined with 1 molecule of the salt in the solution in question.

The results for copper chloride, copper nitrate, aluminium chloride, and aluminium nitrate are given below in Tables LIII. to LVI. m is the concentration in gram-molecular normal, α the dissociation of the solution, L the calculated molecular lowering, $\frac{\Delta}{m}$ the observed molecular lowering, $\frac{\Delta'}{m}$ the corrected or true molecular lowering, m' the number of gram-molecules of water combined with the dissolved substance. These results are plotted in curves, Fig. XVIII., the ordinates representing number of gram-molecules of water combined with the dissolved substance, and the abscissæ concentration of the solution.

A glance at the tables, LIII. to LVI. or the curves in Fig. XVIII., will show that the amount of water combined with 1 molecule of the dissolved substance is greatest in the most

Table LIII.—Copper Chloride.

m.	a.	L.	$\frac{\Delta}{m}$.	$\frac{\Delta'}{m}$.	m'.
2.602	0.137	2.39	8.00	7.65	38.2
2.0816	0.187	2.58	7.43	7.24	35.7
1.8210	0.212	2.68	7.12	6.96	34.2
1.5612	0.238	2.77	6.65	6.48	31.8
1.3010	0.292	3.20	6.45	6.32	27.4
0.7806	0.359	3.23	5.65	5.08	20.2

Table LIV.—Copper Nitrate.

m.	a.	L.	$\frac{\Delta}{m}$.	$\frac{\Delta'}{m}$.	m'.
2.36	0.172	2.53	9.26	8.21	38.4
1.89	0.231	2.75	8.20	7.55	35.3
1.65	0.263	2.87	7.07	5.87	28.4
1.18	0.337	3.15	6.60	6.34	11.0

Table LV.—Aluminium Chloride.

m.	a.	L.	$\frac{\Delta}{m}$.	$\frac{\Delta'}{m}$.	m'.
2.124	0.177	2.88	21.18	19.32	48.1
1.593	0.237	3.22	14.98	14.15	43.7
1.434	0.253	3.31	13.60	13.10	42.0
1.195	0.312	3.64	11.40	11.00	37.2
0.876	0.388	4.07	9.09	8.84	30.0
0.657	0.435	4.33	7.79	7.63	24.0
0.531	0.476	4.56	7.21	7.10	19.8
0.398	0.529	4.86	6.52	6.45	13.7
0.299	0.570	4.91	6.15	5.63	7.1
0.200[1]	0.620	5.38	5.74	5.71	3.3

Table LVI.—Aluminium Nitrate.

m.	a.	L.	$\frac{\Delta}{m}$.	$\frac{\Delta'}{m}$.	m'.
0.066	0.306	3.61	11.06	10.36	36.2
0.853	0.366	3.94	9.60	9.12	31.6
0.746	0.407	4.17	9.06	8.68	29.0
0.533	0.478	4.58	8.00	7.77	23.5
0.320	0.564	5.06	7.15	7.02	15.5
0.213	0.621	5.38	6.57	5.78	3.8

[1] We convinced ourselves that in this determination it was ice and not the solid salt that separated, as follows: As more and more of the solid separated the thermometer sank lower and lower, going down from —45°, the true freezing-point, gradually to —50°. This could not have occurred if the salt was separating either as such or as a hydrate, since the hydrate that would separate could not carry more water with it out of solution than the quantity with which it was combined in solution.

Jones and Getman.
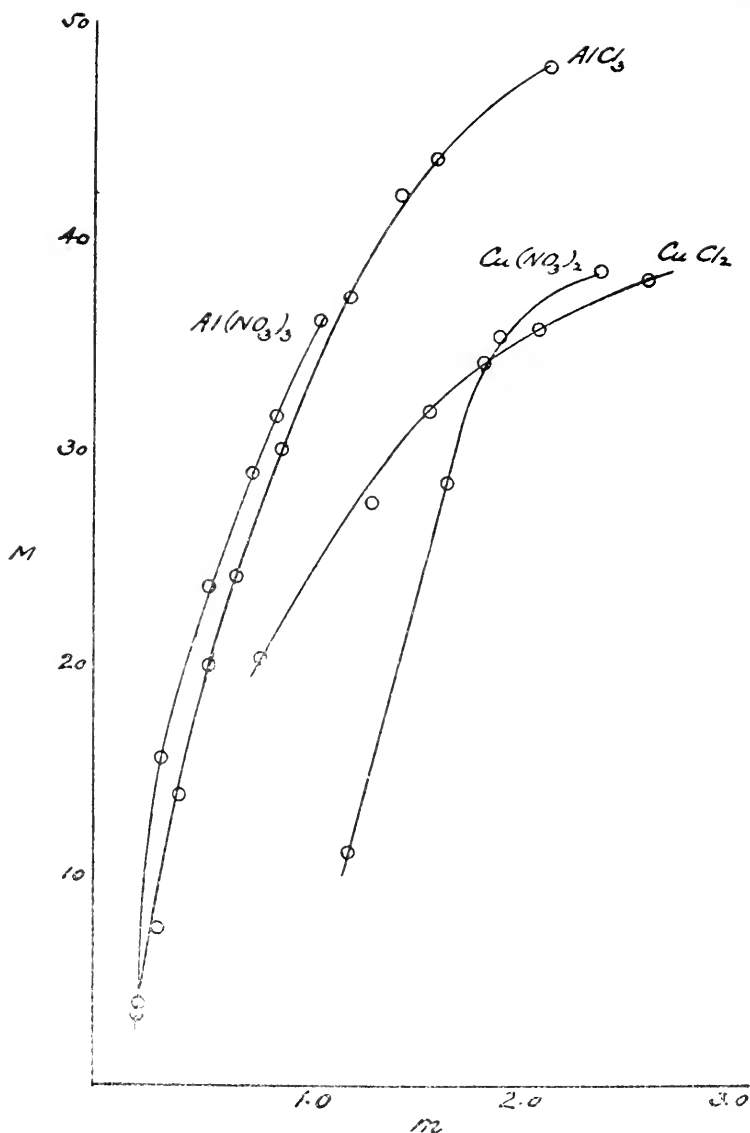
Fig. XVIII.

concentrated solution employed, and becomes less and less as the dilution of the solution increases. The regularity of the

curves expressing the relation between concentration of the solution and composition of the hydrates, is really surprising when we consider the number of experimentally determined quantities involved in every point on the curve. There are no less than four such quantities : (1) The concentration of the solution ; (2) the lowering of the freezing-point ; (3) the specific gravity of the solutions ; (4) the dissociation of the solutions. Quantities (1) and (3) can be measured very accurately. Quantity (2) can be determined with a fair degree of accuracy, but in the most concentrated solutions that we studied there is necessarily some appreciable error involved in measuring the freezing-points. Quantity (4) is the most difficult to measure accurately for such substances as those given in Fig. XVIII., since it involves both the freezing-point and conductivity methods. As has been pointed out, $\mu\infty$ for aluminium chloride and nitrate cannot be determined directly by the conductivity method, on account of the hydrolytic dissociation in dilute solutions. But by continuing the conductivity and freezing-point methods the approximate value of $\mu\infty$ at $0°$ could be obtained. The values of α, involving these values of $\mu\infty$, may, therefore, contain a not inappreciable error.

However, notwithstanding all of these facts, the curves came out as smoothly as could be expected, if they contained only one or two experimentally determined values.

The fact that the amount of water combined with 1 molecule of the salt is greatest in the most concentrated solution, and becomes less and less as the dilution is increased, is just what we would expect. In the dilute solutions there is no evidence of the existence of hydrates. Indeed, there is strong evidence that hydrates of any considerable complexity do not exist. The dissociation of dilute solutions can be measured by the freezing-point method, and also by the conductivity method, and the two methods give the same results within the limits of experimental error. It is impossible that the same results should be obtained from the two methods if there were complex hydrates formed in the dilute solutions.

It is worth while calling attention again, at this point, to

the relation between the complexity of the hydrate formed in solution and the number of molecules of water with which the substance in question crystallizes, since it is so apparent from Fig. XVIII. Aluminium nitrate crystallizes from solution with 8 molecules of water. It contains more water of crystallization in stable combination than any salt that we have studied, with the exception of aluminium sulphate, and we have seen that the sulphates show polymerization in concentrated solutions.

Aluminium chloride and nitrate give greater lowerings of the freezing-point than any other substances that we have studied, and, therefore, form more complex hydrates in concentrated solution than any other substance investigated. Such a general relation is almost more than we could expect, and yet it undoubtedly exists.

Do the Molecules or the Ions Form the Hydrates?

It is difficult to say with certainty whether it is the molecules or the ions, or both, that form the hydrates in concentrated solutions, since all such solutions that we have studied contain both molecules and ions. Since, however, those solutions that are most concentrated, and, therefore, the least dissociated, show the greatest amount of hydration, it seems probable that it is the molecules and not the ions that combine with water and form hydrates. This conclusion is further strengthened by the fact that in the dilute solutions where the number of ions relative to the number of molecules is large, there is little if any hydration.

Taking both of these facts into account, it becomes highly probable that it is the molecules and not the ions that combine with water, forming the hydrates.

Relation to the Work of Roozeboom.

The above results, especially those with aluminium chloride, which have been worked out fully, recall the beautiful investigations of Roozeboom on calcium chloride[1] and ferric chloride.[2] Roozeboom showed that each of these substances

[1] Ztschr. phys. Chem., **4**, 31 (1889).
[2] *Ibid.*, **10**, 477 (1892).

is capable of forming a number of definite hydrates with water, in very concentrated solutions. This, of course, does not prove that such substances form hydrates at the much greater dilutions at which we worked, but is quite in keeping with our theory, and, indeed, furnishes circumstantial evidence in its favor.

Summary.

1. Of the forty-nine electrolytes that we have studied, thirty-nine show a minimum in the freezing-point curve. Nearly all of the forty-nine compounds, whether they do or do not show such a minimum, give too great lowering of the freezing-point of water in concentrated solutions, as calculated from their dissociation, except a few sulphates which were shown to be polymerized in such solutions.

2. The boiling-point curves, as far as they have been worked out, also show a minimum, but this occurs at greater concentration than in the corresponding freezing-point curve.

3. The conductivity curves and the refractivity curves show no sign of a minimum, not even in the regions of concentration where the freezing-point minima and boiling-point minima occur.

4. The theory that has been advanced to account for all of the facts is that in such concentrated solutions the dissolved substance combines with the solvent, forming hydrates. These exist in concentrated solutions together with a relatively small number of ions resulting from the electrolytic dissociation of the salt.

5. It was pointed out that if such hydrates exist in solution, those substances that crystallize from such solutions with the largest amount of water of crystallization, would be the substances, *cæteris paribus*, that we would expect to form the most complex hydrates in such solutions.

6. A careful study of this relation was made, comparing those substances which could reasonably be expected to come within its scope. The comparison would, of course, be limited to the salts of any given acid and to the metals of any given group, or at most to the metals of correlated groups.

The result is that of the thirty-eight substances thus far studied, which have water of crystallization, there is only one apparent exception to this relation, and that exception is not clean cut.

7. It was further pointed out that the fact that the boiling-point minimum occurs at greater concentration than the freezing-point minimum argues strongly in favor of our theory. The hydrates in solution would be less stable at the higher temperature, and, therefore, a greater concentration would be required for their production.

8. Every one of the forty-nine substances studied that crystallizes without water of crystallization, gives relatively small lowering of the freezing-point in concentrated solution, but nearly every one at the same time gives a lowering that is too great as calculated from its dissociation.   These substances, therefore, like those that crystallize with water of crystallization, form hydrates in concentrated solutions, but the hydrates contain much less water, just as we would expect.

9. A freezing-point curve was then carefully studied, and the exact significance of the minimum pointed out—it is the concentration at which the diminishing dissociation is just counterbalanced by the increasing formation of the hydrates with increasing concentration.

10. The composition of the hydrates was then calculated in those cases where sufficient data have already been obtained, and it was found that the hydrates decrease regularly in complexity with the dilution, (Fig. XVIII.) disappearing entirely at a dilution greater than that at which the freezing-point minimum occurs.   The regularity of the curves that were obtained is surprising, considering the number of quantities experimentally determined, that is involved in each point on the curve.

11. Evidence was furnished, indicating that it is the molecules and not the ions, that form the hydrates in concentrated solutions.

Conclusion..

The accusation has been made against the modern theory

of solution, especially by those who do not worship at the shrine of the ion, that it applies only to dilute solutions, and there is a certain justification for the criticism. It has been claimed that the laws of gas-pressure apply only to dilute solutions, and from the data available it seemed that such was the case.

We believe that the explanation of this apparent discrepancy is now at hand. In concentrated solutions a part of the solvent is combined with the dissolved substance, and such solutions are, therefore, more concentrated than they would appear to be from the amount of dissolved substance present in them. When this is taken into account it will probably be shown that the gas laws apply to concentrated solutions as well as to dilute. In making such applications it will probably be necessary to take into account also such factors as appear in Van der Waals' equation for gases, but this would only render still more nearly parallel the gaseous condition and the condition of the dissolved substance.

We shall extend this work as rapidly as possible, bringing a much wider range of substances within its scope, and obtaining such data as are still necessary in order to be able to calculate the composition of the hydrates formed by those substances whose freezing-point lowerings we have already studied, and the change in the composition of such hydrates with change in dilution.

We shall later take up a systematic study of the non-electrolytes from this same standpoint. It is already known that many such substances show abnormally great lowering of the freezing-point of water in concentrated solutions. A systematic study of this field from the standpoint recorded in this paper will probably show that these substances, like the electrolytes, also combine with water in concentrated solutions. This problem also we shall take up as soon as possible.

In conclusion, we wish to thank the Carnegie Institution for the grant which has made possible the rapid prosecution of this work.

ON TETRACHLORDINITROBENZOL.

By C. Loring Jackson and H. A. Carlton.

Our object in undertaking the work described in this paper was to study the behavior of trichlortrinitrobenzol with various reagents. This substance was prepared by Dr. J. F. Wing,[1] in this laboratory, in 1887, without difficulty, but all attempts to make it in recent years have led to low melting products, from which no trichlortrinitrobenzol could be isolated. It was evident that some condition necessary to the formation of the trichlortrinitrobenzol had been overlooked, but even after consultation with Dr. Wing we were unable to recall this condition. Finally, after many experiments, it was found that the missing condition was the use of a return-condenser during the boiling of the trichlordinitrobenzol with nitric and sulphuric acids instead of closing the flask with a porcelain crucible or glass bulb as in the later experiments. With this precaution the trichlortrinitrobenzol becomes again an easily accessible substance.

In the meantime, however, we had turned our attention to the tetrachlordinitrobenzol,[2] as we thought from our experience with the tribromtrinitrobenzol that this might be the impurity formed in our unsuccessful attempts to make the trinitro body, and by the time we had overcome the difficulty in the way of making the trinitro compound we had advanced so far in our work on the tetrachlordinitrobenzol that it was wiser to leave the study of trichlortrinitrobenzol to others.[3]

The tetrachlordinitrobenzol, $C_6Cl_4(NO_2)_2$, was made from unsymmetrical tetrachlorbenzol, and must therefore have the structure $Cl_4 1,3,5,6.(NO_2)_2 2,4$. It melts at 162° and is a decidedly reactive body. With aniline, at 100°, it is converted into the chlortrianilinodinitrobenzol, $C_6(C_6H_5NH)_3Cl(NO_2)_2$, which has a dark red color, melts at 179°, and forms no salts. The constitution of this substance was determined by preparing the tribromchlordinitrobenzol (which melts at 208°) from

ordinary tribromaniline, and treating it with aniline, when it gave the same chlortrianilinodinitrobenzol melting at 179°, thus proving that its structure was

$$(C_6H_5NH)_3 1,3,5.Cl_6,(NO_2)_2 2,4,$$
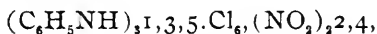
so that the behavior of the tetrachlor compound is the same in this respect as that of the tetrabromdinitrobenzol.[1]

The trichloranilinodinitrobenzol has a most uncommonly strong tendency to form addition-compounds, similar, apparently, to salts with water of crystallization. They were formed by crystallizing the trianiline compound from various solvents, and with the exception of the chloroform compound, were stable in the air or *in vacuo*, but lost the added substance at 100°. A number of substances of this class were prepared, and analyzed, $C_6(Cl_2H_5NH)_3Cl(NO_2)_2C_6H_6$, dark-red, rhombic plates, made by crystallization from benzol. If the crystallization took place from a mixture of ligroin with the smallest possible amount of benzol, orange needles were obtained mixed with some red needles. The orange body gave a loss corresponding to $[C_6(C_6H_5NH)_3Cl(NO_2)_2]_2C_6H_6$. The amount of substance used was so small that we cannot accept this result without additional evidence, but we think this formula may be adopted for the following reasons : The substance was formed when much less benzol was used than that necessary for the red compound just described, and the toluol compound containing 2 molecules of the trianilino compound to 1 of toluol is also orange and crystallizes in needles. It is possible that this compound is an addition-product with the hydrocarbons of the ligroin instead of with benzol, but this does not seem probable to us. We did not provide better analytical results because of the difficulty in separating these orange needles from the red crystals formed with them, which could be done only by mechanical separation. Our attempts to get the red needles in a state of purity failed completely, but an analysis of a mixture of red and orange crystals gave so small a loss that we think these red needles must be the chlortrianilinodinitrobenzol itself.

[1] This JOURNAL, **12**, 294 (1890).

The toluol compound, $[C_6(C_6H_5NH)_3Cl(NO_2)]_2C_7H_8$, formed orange needles. This acetic acid compound was

$$C_6(C_6H_5NH)_3Cl(NO_2)_2C_2H_4O_2,$$
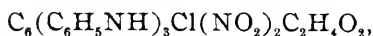
long orange needles ; the chloroform compound,

$$C_6(C_6H_5NH)_3Cl(NO_2)_2CHCl_3,$$
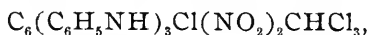
long, dark red narrow prisms. This was the only one of these compounds not permanent in the air. Herman and one of us[1] obtained a similar compound,

$$C_6H(C_6H_5NH)_3(NO_2)_2CHCl_3,$$
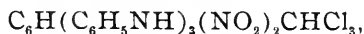
from trianilinodinitrobenzol, but in that work no compound with benzol was observed, and, as the experiments were carried on with care, it seems improbable that one was overlooked.

It was of interest to determine whether the chlortrianilinodinitrobenzol, or rather its addition-compounds occurred in two modifications differing in color like those of the trianilinodinitrobenzol described in the paper just cited. The case of the red and orange needles obtained by crystallizing chlortrianilinodinitrobenzol from ligroin and a little benzol has been discussed already. The acetic acid compound also, when it was first prepared, contained a few red crystals mixed with the orange needles, but all attempts to purify these red needles failed, so we can give no answer to this question.

The action of sodic ethylate on the tetrachlordinitrobenzol consists of two simultaneous reactions. In one three of the atoms of chlorine are replaced by three ethoxy groups,

$$C_6Cl_4(NO_2)_2 + 3C_2H_5ONa = C_6(C_2H_5O)3Cl(NO_2)_2 + 3NaCl,$$
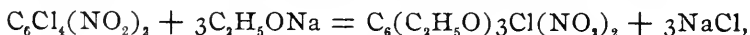
forming what is without much doubt a chlordinitrophloroglucine triethylether, melting at 76°, or the diethylether, $C_6(C_2H_5O)_2OHCl(NO_2)_2$, melting at 102°-103. In the other the two nitro groups are replaced by the two ethoxy groups,

$$C_6Cl_4(NO_2)_2 + 2C_2H_5ONa = C_6Cl_4(C_2H_5O)_2 + 2NaNO_2,$$
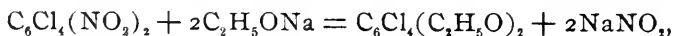
forming tetrachlorresorcine diethylether, melting at 73°. In this respect the behavior of the tetrachlordinitrobenzol with

[1] This JOURNAL, 16, 39 (1894).

sodic ethylate is similar to that of tribromtrinitrobenzol,[1] and probably to that of the tetrabromdinitrobenzol,[2] as the formation of the resorcine ether from this substance has been established, and although the phloroglucine ether has not been isolated, it was undoubtedly formed. There is, however, a marked difference in the behavior of the tetrachlor- and the tetrabromdinitrobenzols, as the latter forms with sodic ethylate $C_6Br_3NO_2(C_2H_5O)_2$, by the replacement of an atom of bromine and a nitro group, instead of undergoing the replacement of both nitro groups, as is the case of the tetrachlor body ; this difference is undoubtedly caused by the weaker attraction of bromine than chlorine for the benzol ring.

Our observations seemed to show that more of the resorcine ether was formed, when the action took place with the aid of heat than in the cold, but this point cannot be considered established until experiments have been tried which are parallel in every other respect. It should also be noted that our work with sodic ethylate has been directed toward the isolation of the principal products of the reaction, not to the identification of all its products.

With sodic malonic ester the tetrachlordinitrobenzol gave trichlordinitrophenylmalonic ester,

$$C_6Cl_3(NO_2)_2CH(COOC_2H_5)_2,$$

melting at 82°, but if the crude product of the reaction was distilled with steam, the residue contained a substance melting at 87°–88°, which gave numbers on analysis corresponding to those for trichlordinitrophenylacetic ester,

$$C_6Cl_3(NO_2)_2CH_2COOC_2H_5,$$
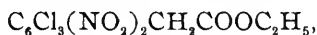
and this yielded on saponification a body analyzing for the trichlordinitrophenylacetic acid, $C_6Cl_3(NO_2)_2CH_2COOH$, and melting at 190°–191°. We have adopted these names for these compounds provisionally, but the second substance differs so much from a substituted acetic acid in its properties that more experimental work is needed on this subject before it can be considered that the value of these bodies is deter-

[1] Jackson and Warren : This JOURNAL, **15**, 608 (1893).
[2] Jackson and Calvert : *Ibid.*, **18**, 311 (1896).

mined with certainty. The most marked peculiarity of this substance is that it does not dissolve in cold aqueous sodic hydrate even with the assistance of a few drops of alcohol, which could hardly be the case if it were an acetic acid. On the other hand, hot sodic or ammonic hydrate forms with it yellow solutions of its salts. It is also unusually stable when boiled with alcohol, showing no tendency to form the ethyl ester like the dichlordinitrophenylacetic acid,[1] or to drop into a substituted toluol under these conditions like the bromdinitrophenylacetic acid.[2] Nor are these peculiarities confined to the substituted acetic acids, since trichlordinitrophenylmalonic ester shows only a very slight tendency to form salts, the trichlordinitrophenylacetic ester none at all, whereas all the other compounds of these classes, which have been studied in this laboratory, form salts very easily. These differences in behavior may be due to the fact that the side chain occupies a different position on the ring in these compounds, or to differences in the side chains themselves, but the real cause of these differences cannot be made out until the constitution of our new compounds has been determined.

Attention is called in the experimental part of the work to some remarkable differences in the amount of heat given off in the reactions of the tetrachlordinitrobenzol with sodic ethylate and with sodic molonic ester as compared with the corresponding reactions with the tetrabromdinitrobenzol, but it is not worth while to discuss these anomalies at present, as the observations were made by different men at considerable intervals of time, and cannot be looked on as established, until they rest on experiments parallel in every respect.

Upon comparing the reaction of the tetrachlordinitrobenzol and sodic malonic ester with the corresponding reaction of tetrabromdinitrobenzol an important difference appears. With the bromine compound 1 atom of bromine is replaced by the malonic ester group and another by hydrogen, forming dibromdinitrophenylmalonic ester, $C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2$, while with the chlorine compound the action stops at the replacement of 1 atom of chlorine by the malonic ester group,

[1] Jackson and Lamar : This JOURNAL, **18**, 682 (1896).
[2] Jackson and Robinson : *Ibid.*, **11**, 551 (1889).

the strange replacement of halogen by hydrogen not taking place, so that the product is

$$C_6Cl_3(NO_2)_2CH(COOC_2H_5)_2.$$

This result was not unexpected, as no such replacement of chlorine by hydrogen has been observed as yet.

<div align="center">EXPERIMENTAL PART.</div>

Preparation of Trichlortrinitrobenzol.

The preparation was carried on as follows: One gram of trichlordinitrobenzol[1] was boiled vigorously for about eight hours in a very long-necked flask with a mixture of 25 cc. of commercial fuming nitric acid of sp. gr. 1.5 and 10 cc. of sulphuric acid of sp. gr. 1.876. The nitric acid used was nearly colorless ; an acid, which owed its high specific gravity to nitrous fumes, would probably not act at all. On cooling, part of the product crystallized out, and the whole was precipitated by pouring the mixture into cold water. The crude precipitate melted at 115°, but one crystallization from alcohol raised it to 185°, and further crystallization brought it to the constant melting-point, 187°, showing that it was the desired symmetrical trichlortrinitrobenzol.

Preparation of Tetrachlordinitrobenzol.

$C_6Cl_4(NO_2)_2,Cl_4,1,3,5,6.(NO_2)_22,4.$—This substance was made from trichloraniline prepared according to Victor Meyer and Sudborough,[2] as follows : One hundred grams of freshly distilled aniline were dissolved in a kilogram of chloroform, which had been washed until free from alcohol and thoroughly dried with calcic chloride. A stream of dry chlorine was passed through the mixture for about thirty hours, the vessel being kept cold by immersion in ice-water. The precipitate formed was filtered out, dried, and washed with water. Yield of trichloraniline 116 grams from 100 grams of aniline, that is 55 per cent of the theoretical yield.

The trichloraniline was converted into tetrachlorbenzol by Sandmeyer's reaction. Twenty grams of trichloraniline were

[1] Jackson and Lamar: This JOURNAL, **18**, 666 (1896).
[2] Ber. d. chem. Ges., **27**, 3151 (1894).

mixed with 120 cc. of strong hydrochloric acid in an Erlenmeyer flask, and 20 grams of powdered sodic nitrite added in small portions at a time, the flask being closed with a glass bulb, and immersed in cold water. When all of the sodic nitrite had been added, the dark brown solution of the diazo compound was treated with 40 grams of cuprous chloride, which caused a considerable effervescence accompanied by a great rise in temperature. After the effervescence had ceased the flask was heated on the steam-bath for two or three minutes. As the solution cooled, part of the tetrachlorbenzol was deposited as a mass of tarry needles. The whole of it was then precipitated by the addition of a large amount of cold water, and purified by crystallization from alcohol.

Twenty grams of trichloranile gave 13.5 grams of tetrachlorbenzol, a yield of 61 per cent of the theoretical.

The tetrachlorbenzol was converted into tetrachlordinitrobenzol, as follows : Twenty grams of it were boiled with a mixture of 200 cc. of fuming nitric acid of sp. gr. 1.5 and 80 cc. of sulphuric acid of sp. gr. 1.84 in an Erlenmeyer flask closed by a loosely fitting glass bulb. After vigorous boiling for half an hour the tetrachlordinitrobenzol began to separate, but disregarding this, the boiling was continued for half an hour longer, and then the contents of the flask were poured into a large amount of cold water. The precipitate thus obtained was crystallized from 90 per cent acetic acid, until it showed the constant melting-point 162°, when it was dried at 100° and analyzed with the following results :

I. 0.1850 gram substance gave, by the Carius method, 0.3496 gram AgCl.

II. 0.1958 gram substance gave 0.3701 gram AgCl.

III. 0.2044 gram substance gave 0.3850 gram AgCl.

IV. 0.1845 gram substance gave 15.3 cc. moist N_2 at 21° and 762 mm.

	Calculated for $C_6Cl_4(NO_2)_2$.	I.	II.	III.	IV.
Cl	46.40	46.72	46.73	46.59	....
N	9.15	....	....	....	9.46

There is no doubt, therefore, that the substance is a tetra-

chlordinitrobenzol and the method of preparation settles its constitution as $Cl,1,3,5,6.(NO_2)_2 2,4$.

Properties of Tetrachlorainitrobenzol. — It crystallizes in thick, white, rhombic plates, which seem to be prisms with much developed basal planes. In some cases each obtuse angle is truncated by a plane, more usually it is bevelled by two planes at a still more obtuse angle. It melts at 162°, and is freely soluble in ether, benzol, chloroform, acetone, or carbonic disulphide; slightly soluble in cold glacial acetic acid, freely soluble in it when hot; essentially insoluble in cold, and only slightly soluble in hot ethyl alcohol; insoluble in water. The best solvent for it is 90 per cent hot acetic acid. It is not affected by the three strong acids or sodic hydrate. It is a decidedly stable substance, as heating to 300° for two days with fuming nitric acid was necessary to decompose it, and it can be heated to its boiling-point without decomposition, and is decomposed only very slowly by prolonged boiling.

Action of Aniline on Tetrachlordinitrobenzol.

Chlortrianilinoditrobenzol, $C_6(C_6H_5NH)_3Cl(NO_2)_2$. — Five grams of tetrachlordinitrobenzol were mixed with 50 grams of freshly distilled aniline, and heated on the steam-bath. The cold aniline dissolved but little of the tetrachlordinitrobenzol, on heating for a short time, however, the whole dissolved with a red color, which grew much darker as the heating continued. The large excess of aniline was necessary to keep the substance in solution. After heating for three hours the product was allowed to cool, when a mass of dark red needles was deposited. The excess of aniline was removed by treatment with dilute hydrochloric acid and the dark red residue filtered off, washed thoroughly with water, and purified by crystallization from a mixture of ligroin and benzol, until it showed the constant melting-point 179°, when it was dried at 100° and analyzed with the following result:

I. 0.1958 gram substance gave, by the Carius method, 0.0604 gram AgCl.

II. 0.1971 gram substance gave 26.2 cc. of moist N_2 at 28° and 770 mm.

	Calculated for $C_6(C_6H_5NH)_3Cl(NO_2)_2$.	Found.	
		I.	II.
Cl	7.46	7.63	. . . .
N	14.72	. . . .	14.79

The substance is therefore the chlortrianilinodinitrobenzol formed by replacing three of the atoms of chlorine by three aniline groups.

Properties of the Chlortrianilinodinitrobenzol.—We are unable to give the crystalline form of this substance, as it is separated from each of the solutions tried by us in the form of an addition-compound with the solvent. From a mixture of much ligroin with little benzol a few red needles were obtained, which may have been the chlortrianilinodinitrobenzol, but we were unable to prove that this was the case. It has a dark red color, and melts at 179°. It is freely soluble in ether, chloroform, acetone, or carbonic disulphide ; soluble in cold benzol, or glacial acetic acid, freely soluble in these solvents, when hot ; slightly soluble in ethyl alcohol, whether cold or hot, somewhat more soluble in methyl alcohol ; insoluble in cold ligroin, only slightly soluble in it when hot; insoluble in water. There is no good solvent for it on account of its tendency to combine with the most various solvents. Aniline or acetol also dissolves it, but seems to form addition-compounds like the other solvents studied. Neither strong hydrochloric acid, nor strong nitric acid has any apparent action on it. A more particular account of its behavior with hydrochloric acid is given later. Strong sulphuric acid decomposes it even in the cold. Sodic hydrate in aqueous solution has no action on it. Further treatment with aniline failed to remove the fourth atom of chlorine. Its most striking property is its very strong tendency to form addition-compounds, in which the added body seems to have the same function as water of crystallization. Some of these substances are described below.

Compounds of Chlortrianilinodinitrobenzol with Benzol.

$C_6(C_6H_5NH)_3Cl(NO_2)_2.C_6H_6.$—This substance, obtained by crystallizing chlortrianilinodinitrobenzol from benzol, gave the following results on analysis :

I. 0.3373 gram of the air-dried substance, when heated to 100°, lost 0.0475 gram.

II. 0.3435 gram lost 0.0485 gram.

III. 0.2026 gram of substance dried *in vacuo* gave 23.5 cc. of moist N_2 at a temperature of 26° and a pressure of 755 mm.

IV. 0.1709 gram of substance dried *in vacuo* gave, by the Carius method, 0.0450 gram AgCl.

	Calculated for $C_6Cl(C_6H_5NH)_3(NO_2)_2C_6H_6$.	I.	Found. II.	III.	IV.
C_6H_6	14.09	14.08	14.11	....	....
N	12.65	....	....	12.79	....
Cl	6.41	....	....	....	6.57

There can be no doubt therefore that the substance is composed of one molecule of the chlortrianilinodinitrobenzol and one of benzol.

Properties.—It forms dark crimson rhombic plates. It melts at the same temperature as the chlortrianilinodinitrobenzol, 179°, as it is broken up by heat. At ordinary temperatures it is decidedly stable, losing its benzol very slowly even *in vacuo*, but at a temperature of 100° drives off the benzol completely. It seems to be rather less soluble in benzol than the chlortrianilinodinitrobenzol. Other solvents decompose it, giving the addition-compound with the substance used.

$[C_6(C_6H_5NH)_3Cl(NO_2)]_2C_6H_6$.—If the chlortrianilinodinitrobenzol was crystallized from a mixture of benzol and ligroin, orange crystals were obtained, mixed with a dark red substance, and, if the amount of benzol was reduced so that there was barely enough to effect the solution, the crystals were nearly all of the orange form. These orange needles were separated mechanically from the few red needles with which they were mixed, and analyzed with the following result :

0.1310 gram air-dried substance, when heated to 100°, lost 0.0103 gram.

	Calculated for $[C_6(C_6H_5NH)_3Cl(NO_2)_2]_2C_6H_6$.	Found.
C_6H_6	7.58	7.86

This analysis cannot be accepted as establishing with certainty the existence of the compound of 2 molecules of the

anilino body with 1 of benzol. In the first place the amount
of substance used was so small that the analysis must be re-
garded with suspicion, and the difficulty of obtaining it was
so great that we have not repeated it with larger quantities.
Secondly, it is possible that this compound contains a paraffin
hydrocarbon from the ligroin instead of benzol, but we think
that the formula given above may be accepted for this sub-
stance with safety in view of the strong similarity between it
and the toluol compound, which follows, whose composition
has been established with certainty. The red crystals ob-
tained from benzol and ligroin seemed to be crystals of
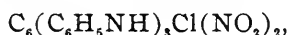
$$C_6(C_6H_5NH)_3Cl(NO_2)_2,$$

to judge from an analysis of a mixture of them and the orange
substance, but we could not get them pure enough to settle
this point.

Compound of Chlortrianilinodinitrobenzol with Toluol,
$(C_6(C_6H_5NH)_3Cl(NO_2)_2)_2C_7H_8$.—This substance, prepared by
crystallizing the trianilino body from toluol, gave the follow-
ing results on analysis :

I. 0.3386 gram air-dried substance, when heated to 120°,
lost 0.0306 gram.

II. 0.3222 gram substance lost 0.0287 gram.

III. 0.3410 gram substance lost 0.0308 gram.

	Calculated for $(C_6Cl(C_6H_5NH)_3(NO_2)_2)_2C_7H_8$.	I.	Found. II.	III.
C_7H_8	8.82	9.04	8.90	9.03

The substance is therefore a compound of 2 molecules of
the anilino body wtih 1 of toluol. The compound

$$C_6(C_6H_5NH)_3Cl(NO_2)_2C_7H_8$$
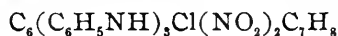
would contain 16.21 per cent of toluol. That it has a con-
stant composition is shown by the fact that two of the analy-
ses (I. and III.) were made with samples from different prepa-
rations.

Properties.—It crystallizes in clusters of brilliant orange
needles, which are stable at ordinary temperatures, since
0.3386 gram of the substance lost nothing on standing for a

day in the air, and only 0.0010 gram after two days *in vacuo*. When heated it loses its toluol, the color changing from orange to the dark red of the chlortrianilinodinitrobenzol. The toluol was identified by its smell and combustibility. It is somewhat less soluble in toluol than the mother substance. This compound, like all the other addition-compounds described in this paper, cannot be obtained by allowing the solvent to stand with the solid chlortrianilinodinitrobenzol, but appears only when it is crystallized from a solution.

Compound of Chlortrianilinodinitrobenzol with Acetic Acid, $C_6(C_6H_5NH)_3Cl(NO_2)_2C_2H_4O_2$.—This substance was made by crystallizing the anilino body from glacial acetic acid. It could also be obtained from the benzol addition-compound by crystallization from glacial acetic acid. The product consisted principally of long, orange needles mixed with a small amount of red needles, from which they were separated mechanically, and analyzed with the following results:

I. 0.3465 gram air-dried substance, when heated to 130°, lost 0.363 gram.

II. 0.1390 gram substance lost 0.0159 gram.

III. 0.3303 gram substance lost 0.0353 gram.

IV. 0.3305 gram substance lost 0.0381 gram.

V. 0.1720 gram air-dried substance gave, by the Carius method, 0.0471 gram AgCl.

	Calculated for $C_6Cl(C_6H_5NH)_3(NO_2)_2C_2H_4O_2$.	I.	II.	Found. III.	IV.	V.
$C_2H_4O_2$	11.20	10.47	11.44	10.69	11.53	....
Cl	6.62	....	....	....	....	6.77

The substance is therefore formed by the union of 1 molecule of acetic acid with 1 of the chlortrianilinodinitrobenzol. In order to show that the heat acted only by driving off the acetic acid, the residue dried at 130° was analyzed with the following result:

0.1780 gram substance gave, by the Carius method, 0.0542 gram AgCl.

	Calculated for $C_6Cl(C_6H_5NH)_3(NO_2)_2$.	Found.
Cl	7.46	7.53

An attempt was also made to isolate the red needles formed with the orange crystals on crystallizing chlortrianilinodinitrobenzol from acetic acid. They were carefully mixed out from the mixture and recrystallized from a small amount of acetic acid, but the product again consisted of a mixture of orange and red needles, so that in spite of repeated efforts we did not succeed in getting the red product pure. We cannot, therefore, decide definitely the question, whether this acetic acid compound occurs in two modifications. One opinion is that the orange body is the only form, the red crystals being probably the chlortrianilinodinitrobenzol without acetic acid of crystallization, and this view is supported by the fact that, if crystallized in a beaker, most of the product consists of the orange needles. If, on the other hand, it is crystallized in a watchglass, where portions of it crystallizes in contact with less acetic acid, the red crystals are formed in considerable quantity.

Properties of $C_6(C_6H_5NH)_3Cl(NO_2)_2C_2H_4O_2$.—It crystallizes in long, orange needles, and is stable at ordinary temperatures, but loses its acetic acid rapidly when heated, changing color from orange to dark red. It is less soluble in acetic acid than the mother-substance. Other solvents decompose it, giving the compound of the anilino body with the solvent used.

Compound of Chlortrianilinodinitrobenzol with Chloroform, $C_6(C_6H_5NH)_3Cl(NO_2)_2CHCl_3$.—This substance was prepared by crystallizing the chlortrianilinodinitrobenzol from chloroform, to which a little ligroin had been added, as it comes down as a varnish, if chloroform alone is used. As it proved to be decidedly unstable, it was prepared for analysis simply by pressure in filter-paper.

I. 0.2845 gram substance, when heated to 100°, lost 0.0520 gram.

II. 0.4165 gram substance lost 0.0906 gram.

III. 0.3389 gram substance lost 0.0624 gram.

IV. 0.1283 gram substance lost 0.0253 gram.

	Calculated for $C_6(C_6H_5NH)_3Cl(NO_2)_2CHCl_3$.	I.	II.	III.	IV.
			Found.		
$CHCl_3$	20.08	18.28	21.75	18.41	19.72

These analyses leave much to be desired, but are perhaps as near as could be expected with a substance that gives off chloroform rapidly at ordinary temperatures. They leave no doubt as to the formula of the substance. We may add that the presence of the chloroform in it was proved by the isonitrile test with aniline and sodic hydrate.

Properties of $C_6(C_6H_5NH)_3Cl(NO)_2CHCl_3$.—It crystallizes from chloroform in dark-red, long, narrow prisms, terminated at each end by two planes at a right angle to each other. It is the least stable of these compounds studied by us, since it gives off chloroform even at ordinary temperatures. It is less soluble in chloroform than the mother-substance. Other solvents decompose it, giving the compound with the solvent used.

Attempts to Prepare the Chloride of Chlortrianilinodinitrobenzol.—Although substances closely related to this do not usually give chlorides, we thought that special experiments should be tried in this direction in view of the strong tendency to form addition-compounds shown by the chlortrianilinodinitrobenzol. Accordingly, some of it was dissolved in anhydrous benzol and treated with dry hydrochloric acid gas. A red precipitate was formed, but this was proved by analysis to be the compound with benzol.

I. 0.3445 gram air-dried substance, when heated to 100°, lost 0.0502 gram.

II. 0.1772 gram substance gave, by the Carius method, 0.0468 gram AgBr.

	Calculated for $C_6(C_6H_5NH)_3Cl(NO_2)_2C_6H_6$.	Found. I.	II.
C_6H_6	14.09	14.57	....
Cl	6.41	....	6.53

In a second experiment some chlortrianilinodinitrobenzol was dissolved in acetone and mixed with strong hydrochloric acid (the laboratory reagent). A dark-red precipitate was formed, which, however, was nothing but the chlortrianilinodinitrobenzol, as it melted at 179° and lost nothing when heated for some time to 130°.

Constitution of Chlortrianilinodinitrobenzol.—Judging from analogy, there can be little doubt that the atom of chlorine in the chlortrianilinodinitrobenzol stands in the meta position to the two nitro groups, but in order to place our knowledge of the structure on an experimental basis we made the chlortribromdinitrobenzol, $Br_3 1,3,5.Cl6.(NO_2)_2 2,4$, and converted this into a chlortrianilinodinitrobenzol, which proved to be indentical with the one from the tetrachlordinitrobenzol, showing that its constitution is $(C_6H_5NH)_3 1,3,5.Cl6.(NO_2)_2 2,4$.

The tribromaniline used by us was prepared in the usual way[1] by passing a stream of air saturated with bromine vapor through a dilute solution of chloride of aniline. The precipitate of tribromaniline was washed with water and used without further purification. An analysis showed that it was pure. The tribromchlorbenzol was prepared from it by Sandmeyer's reaction, as this seemed more convenient than the method of preparation of Langer[2] or Silberstein.[3] Ten grams of tribromaniline were mixed with 70 cc. of strong hydrochloric acid, and then 6.3 grams of sodic nitrite were added in small portions at a time, the flask being immersed in cold water. The dark-brown diazo solution was then treated with 12 grams of cuprous chloride, and, after the effervescence had ceased, the mixture 1 e ated for two or three minutes on the steambath. After it had cooled, the gray precipitate was dried on a porous plate and was pure enough for our purpose without further treatment. In this way 9 grams of tribromchlorbenzol were obtained from 10 grams of tribromaniline, a yield of 85 per cent. The tribromchlorbenzol prepared in this way melted at 90° to 91°, that is nearly 10° higher than the melting-points ascribed to it by Silberstein, 80°, or Langer, 82°. This difference seems to be due to an obstinately adhering impurity in the product prepared by the older methods of applying the diazo reaction, for a product made by the action of hydrochloric acid on the diazo salt in acetic acid[4] melted as low as 65°, and was raised even to 82° only by long-continued

[1] This JOURNAL, **21**, 518 (1899).
[2] Ann. Chem. (Liebig), **215**, 113 (1882).
[3] J. prakt. Chem., [2], **27**, 115 (1883).
[4] Jackson and Calvert : This JOURNAL, **18**, 309 (1896).

recrystallization. That our product melting at 90° to 91° was pure is shown by the following analysis :

0.1871 gram substance gave, by the Carius method, 0.3760 gram mixture AgCl and AgBr.

	Calculated for $C_6H_2Br_3Cl$.	Found.
Br	78.79	78.18

There can be no doubt, therefore, that the true melting-point of the tribromchlorbenzol is 90° to 91°.

To prepare the tribromchlordinitrobenzol, 7 grams of the tribromchlorbenzol were boiled for half an hour with a mixture of 70 cc. of fuming nitric acid of sp. gr. 1.4 and 28 cc. of sulphuric acid of sp. gr. 1.84 in an Erlenmeyer flask, loosely closed with a glass bulb. The tribromchlorbenzol melted to a brown oil at first, and after boiling for about five minutes the tribromchlordinitrobenzol began to separate in crystals. After the liquid had cooled the substance was filtered out through glass wool and purified by crystallization from glacial acetic acid until it showed the constant melting-point 208°, when it was dried at 100° and analyzed with the following result :

I. 0.1549 gram substance gave, by the Carius method, 0.2505 gram AgCl + AgBr.

II. 0.3311 gram substance gave 19.0 cc. moist N_2 at 23°.5 and 768 mm.

	Calculated for $C_6Br_3Cl(NO_2)_2$.	Found. I.	II.
Br + Cl	62.66	62.96	....
N	6.37	....	6.52

Properties of Tribromchlordinitrobenzol,

$Br_3 1,3,5.Cl_6.(NO_2)_2 2,4$.—It crystallizes from benzol in white, square-ended prisms usually so short that they look like cubes, from glacial acetic acid in irregular rhombic forms, resembling those of the tetrachlordinitrobenzol. It melts at 208°, and is freely soluble in ether, benzol, chloroform, acetone, or carbonic disulphide ; slightly soluble in cold glacial acetic acid, freely soluble in it when hot ; essentially insoluble in cold alcohol or ligroin, slightly soluble when hot ; in-

soluble in water. The best solvent for it is glacial acetic acid. The three strong acids do not affect it, nor does sodic hydrate in aqueous solution. It is decomposed with great difficulty, even by fuming nitric acid at high temperatures, and can be boiled for some time with but slight decomposition. Its properties, therefore, resemble most closely those of the tetrachlordinitrobenzol.

One gram of the tribromchlordinitrobenzol was mixed with 10 grams of freshly distilled aniline. It only dissolved partially in the cold, but on heating on the steam-bath solution took place, and the liquid became dark-red. After the heating had been continued for three hours the excess of aniline was removed with dilute hydrochloric acid and the thoroughly washed precipitate crystallized from a mixture of ligroin and benzol, until it showed a constant melting-point. As this lay at 179°, it was evident that the product was the same chlortrianilinodinitrobenzol as that made from tetrachlordinitrobenzol. For greater safety the substance was analyzed.

0.2008 gram substance gave, by the Carius method, 0.0606 gram AgCl.

	Calculated for $C_6(C_6H_5NH)_3Cl(NO_2)_2$.	Found.
Cl	7.46	7.46

Before carrying out this method of proving the structure of the chlortrianilinodinitrobenzol we tried to reach the same end by converting it into the trianilinodiaminobenzol and comparing this with a preparation of known structure, but the difficulty of handling the trianilinodiaminobenzol caused us to abandon this method for the easier one just described.

Action of Sodic Ethylate in the Cold on Tetrachlordinitrobenzol.

Ten grams of the tetrachlordinitrobenzol were dissolved in 20 cc. of anhydrous benzol and mixed with the solution of sodic ethylate prepared by treating 3.17 grams of sodium with 80 cc. of absolute alcohol, that is a little more than 4 molecules of ethylate to each molecule of the dinitro compound. The mixture was kept cold by immersing the flask in ice during the first part of the operation, as it was found the reaction

was accompanied with a considerable rise of temperature.
As soon as the ethylate was added an orange-red color appeared, and a white precipitate of sodic chloride and nitrite
began to form.   After fifteen minutes the reaction seemed to
have come to an end, as no more of the precipitate was formed,
and there was no further perceptible rise in temperature, but
in order to made sure that it was complete the mixture was
allowed to stand in a corked flask at ordinary temperatures for
two days.   The liquid was then allowed to evaporate spontaneously, and the orange-red residue treated with cold water,
which gave a deep red solution, and left behind a light-red,
pasty mass.   The latter was filtered out, washed thoroughly
with water, and recrystallized from alcohol until it showed the
constant melting-point 76°, when it was dried *in vacuo* and
analyzed with the following results :

I. 0.2065 gram substance gave, by the Carius method,
0.0925 gram AgCl.

II. 0.2005 gram substance gave 0.0883 gram AgCl.

III. 0.3047 gram substance gave 23.4 cc. moist N_2 at 24°.5
and 7.64 mm.

	Calculated for $C_6(C_2H_5O)_3Cl(NO_2)_2$.	I.	Found. II.	III.
Cl	10.61	11.08	10.88	....
N	8.37	....	....	8.64

The substance therefore was formed by the replacement of
three of the atoms of chlorine by three ethoxy groups, judging from the structure of the trianilino body, is undoubtedly
chlordinitrophloroglucine triethyl ether.

Properties of the Chlordinitrophloroglucine Triethyl Ether.—
It crystallizes from alcohol in long, flat, white needles, usually
terminated by one plane at an oblique angle to the sides,
rarely by two planes.   These crystals show a tendency to
unite in parallel groups ; radiating groups were not observed.
It gradually turns dark on exposure to sunlight.   It melts at
76° and is freely soluble in ether, benzol, chloroform, acetone,
glacial acetic acid, or carbonic disulphide ; slightly soluble in
cold alcohol, freely soluble in it when hot ; essentially insoluble in cold ligroin, moderately soluble in it when hot ; essen-

tially insoluble in cold water; slightly soluble in hot water. Boiling sulphuric acid of sp. gr. 1.44 has little action on it, but a boiling dilute solution of sodic hydrate saponifies it, giving an orange-red solution, from which hydrochloric acid throws down a yellow phenol.

The dark-red, aqueous filtrate, which had been separated from the crude chlordinitrophloroglucine triethyl ether, was acidified with hydrochloric acid, and the yellow, oily precipitate thus obtained was allowed to stand for a day or two on filter-paper, which absorbed most of the oil. We can give no account of the nature of the oil extracted afterward from the paper. The more solid product could now be crystallized from ligroin, and after repeating this crystallization several times the purification was finished by recrystallization from a mixture of alcohol and water until it showed the constant melting-point 102° to 103°, when it was dried *in vacuo* and analyzed with the following results:

I. 0.1551 gram substance gave, by the Carius method, 0.0767 gram AgCl.

II. 0.1661 gram substance gave 14.0 cc. moist N_2 at 25° and 759 mm.

	Calculated for $C_6(C_2H_5O)_2OHCl(NO_2)_2$.	Found. I.	Found. II.
Cl	11.58	12.25	....
N	9.14	....	9.34

The substance is therefore the diethyl ether, formed probably by partial saponification of the chlordinitrophloroglucine triethyl ether.

Properties of Chlordinitrophloroglucine Diethyl Ether, $C_6(C_2H_5O)_2OHCl(NO_2)_2$.—It crystallizes from dilute alcohol in slender, yellow needles with very long, pointed ends; they are often somewhat branched. It melts at 102° to 103°, and is freely soluble in alcohol, ether, benzol, acetone, chloroform, glacial acetic acid, or carbonic disulphide; slightly soluble in cold ligroin, easily soluble in hot; essentially insoluble in cold water, only slightly soluble in it when hot. It dissolves in sodic hydrate, giving an orange solution of the sodium salt. The ammonium salt, made by dissolving the

ether in an excess of ammonic hydrate and warming gently
till free from ammonia, gave the following precipitates :

> Baric chloride, a yellow precipitate ;
> Plumbic acetate, an orange precipitate ;
> Ferric chloride, a white precipitate.

No precipitates were obtained with argentic nitrate or
cupric sulphate.

Barium Salt of the Chlordinitrophloroglucine Diethyl Ether,
$[C_6(C_2H_5O)_2Cl(NO_2)_2O]_2Ba$.—The salt was made by adding
baric chloride to the ammonium salt of the diethyl ether. It
was purified by washing with water, dried at 120° and analyzed
with the following result :

o.1781 gram salt gave, by evaporation with sulphuric acid,
0.0543 gram $BaSO_4$.

	Calculated for $[C_6(C_2H_5O)_2Cl(NO_2)_2O]_2Ba$.	Found.
Ba	18.31	17.93

Properties of the Barium Salt.—It crystallized from water in
small, light-yellow needles, which probably contain water of
crystallization, as they turn to a dark-yellow color in a desic-
cator, or when heated. It is essentially insoluble in cold
water ; moderately soluble in hot ; insoluble in cold alcohol,
only slightly soluble in hot ; insoluble in the other organic
solvents.

Action of Hot Sodic Ethylate on Tetrachlordinitrobenzol.

Ten grams of tetrachlordinitrobenzol, dissolved in benzol,
were treated with a solution of sodic ethylate made from 3.17
grams of sodium and 55 cc. of absolute alcohol, that is about
4 molecules of ethylate to each molecule of the dinitro com-
pound, but the solution of ethylate contained less alcohol than
in the previous experiments in the cold. The liquid turned
orange-red immediately, and deposited a white precipitate of
sodic nitrite and chloride. The temperature also rose as much
as 25°, whereas the corresponding work[1] with tetrabromdini-
trobenzol no evolution of heat was observed. After the addi-
tion of the ethylate the mixture was boiled for ten minutes in

[1] This JOURNAL, **18**, 311 (1896).

a flask with a return-condenser. The solvents were then allowed to evaporate spontaneously, and the orange-red solid treated with water, which separated it into a dark-red solution and a pasty solid. The solution, on acidification with hydrochloric acid, gave a much more oily precipitate than that from the process carried on in the cold. As it could not be crystallized directly, it was treated with ammonic hydrate, and, after the excess of ammonia had been driven off, precipitated with baric chloride. The washed barium salt, on decomposition with dilute hydrochloric acid, yielded a yellow phenol, easily purified by crystallization from either ligroin or dilute alcohol. As it showed the constant melting-point 102° to 103°, it was the chlordinitrophloroglucine diethyl ether,

$$C_6(C_2H_5O)_2OHCl(NO_2)_2,$$

just described.

The substance insoluble in water, remaining after the sodium salt of the diethyl ether had been filtered off, was so oily that it could not be recrystallized. We accordingly distilled it with steam, when a light-yellow oil passed over, which was separated from the water and boiled for three hours with an alcoholic solution of potassic hydrate, as previous experiments had shown us that good results were obtained in this way. The dark-red solution formed deposited, on cooling, a mass of reddish crystals, the quantity of which was much increased by the addition of a large amount of water. The product thus obtained was purified by crystallization from alcohol until it showed the constant melting-point 73°, when it was dried *in vacuo* and analyzed with the following results :

I. 0.1806 gram substance gave, on combustion, 0.2632 gram CO_2 and 0.0618 gram H_2O.

II. 0.1814 gram substance gave, by the Carius method, 0.3433 gram AgCl.

III. 0.1480 gram substance gave 0.2804 gram AgCl.

	Calculated for $C_6Cl_4(C_2H_5O)_2$.	I.	Found. II.	III.
C	39·47	39·75	....	....
H	3·29	3·83	....	....
Cl	46.71	....	46.80	46.85

The substance is therefore the tetrachlorresorcine diethyl ether formed by the replacement of the two nitro by two ethoxy groups.

Properties of Tetrachlorresorcine Diethyl Ether,
$C_6Cl_4(C_2H_5O)_2$.—It crystallizes from alcohol in very slender, pointed, white needles in thick masses, the needles lying nearly, but not quite, parallel to each other. It melts at 73°, and is freely soluble in ether, benzol, chloroform, ligroin, acetone, glacial acetic acid, or carbonic disulphide ; slightly soluble in cold alcohol, freely soluble in it hot ; insoluble in water. It is not affected, apparently, by the three strong acids, or sodic hydrate.

On evaporating the filtrate from the crude tetrachlorresorcine diethyl ether a small quantity of yellow needles was obtained, which exploded on heating. On acidification they yielded the chlordinitrophloroglucine diethyl ether recognized by the constant melting-point 102° to 103°, and were therefore its potassium salt.

The quantities used in these experiments with sodic ethylate, whether hot or cold, were too small to allow the isolation of all the products of the reaction. The substances described are only the compounds, which are formed in the largest amount.

Action of Sodic Malonic Ester on Tetrachlordinitrobenzol.

Trichlordinitrophenylmalonic Ester,
$C_6Cl_3(NO_2)_2CH(COOC_2H_5)_2$.—Five grams of tetrachlordinitrobenzol were dissolved in 10 cc. of anhydrous benzol and mixed with the sodic malonic ester prepared from 5.1 grams of malonic ester and the sodic ethylate from 0.71 gram of sodium and 28 cc. of absolute alcohol. The mixture took on at once a dark-reddish color and a white precipitate began to form, but there was no perceptible evolution of heat, whereas the mixture of sodic malonic ester and tetrabromdinitrobenzol became so hot that it could not be comfortably held in the hand.[1] The mixture was allowed to stand for twenty-four hours at ordinary temperatures in a corked flask and then poured into

[1] This JOURNAL, **12**, 296 (1890).

five times its volume of water acidified with dilute sulphuric acid. The yellow oil precipitated was separated from the water and the benzol allowed to evaporate spontaneously. The oily residue was dissolved in a little hot alcohol, which, on cooling, deposited an oil, but in the course of an hour this partially acidified in small, white crystals, which were washed with cold alcohol till free from adhering oil, and then recrystallized from hot alcohol until they showed the constant melting point 82°, when they were dried *in vacuo* and analyzed with the following results :

I. 0.1770 gram substance gave, on combustion, 0.2368 gram CO_2 and 0.0503 gram H_2O.

II. 0.1607 gram substance gave, by the Carius method, 9.1608 gram AgCl.

	Calculated for $C_6Cl_3(NO_2)_2CH(COOC_2H_5)_2$.	Found.	
		I.	II.
C	36.32	36.49	....
H	2.56	3.18	....
Cl	24.74	....	24.75

The substance is therefore the trichlordinitrophenylmalonic ester.

Properties of Trichlordinitrophenylmalonic Ester.—It crystallizes from alcohol in well developed, white, short, stout prisms terminated either by one plane at a somewhat oblique angle, or by two making an obtuse angle with each other, but these principal planes are modified by many smaller planes. It melts at 82°. One one occasion the melting-point of a sample was found to be 85° to 86°, but after one recrystallization the usual melting-point 82°, was obtained, and we have not succeeded in obtaining again a substance with this higher melting-point. This observation may indicate that the substance occurs in two modifications like those of the trinitrophenylmalonic ester observed by Phinney and one of us,[1] but this influence cannot be accepted without confirmation by further experiment, which we are unable to give. It is freely soluble in ether, benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide ; slightly soluble in cold

[1] This JOURNAL, **21**, 418 (1899).

ethyl or methyl alcohol, freely soluble in either of these solvents, when hot ; essentially insoluble in cold ligroin, soluble in hot ; insoluble in water. Cold hydrochloric acid or cold nitric acid does not dissolve it, but hot nitric acid dissolves it, and so does cold sulphuric acid. Sodic hydrate in aqueous or even in alcoholic solution has little action on it, giving only a slight red color, and not dissolving it. This behavior is entirely different from that of the other substituted phenylmalonic esters studied in this laboratory, which give red solutions of their salts even with aqueous sodic hydrate.

Trichlordinitrophenylacetic Ester,[1]

$C_6Cl_3(NO_2)_2CH_2COOC_2H_5$. — The yield of trichlordinitrophenylmalonic ester by the process described in the preceding section was very small, only 0.5 grams from 5 grams of the tetrachlordinitrobenzol. The reason was obviously that most of the substance remained dissolved in the excess of malonic ester (and perhaps also in the oily secondary products of the reaction), and was taken up by the alcohol used in treating the crude product. In order to obtain this part of the ester, the oil obtained from the evaporation of the alcohol washings was distilled with steam, and, when no more malonic ester passed over, the contents of the flask were allowed to cool and then poured into a large quantity of water. The precipitated oil, after being stirred for some time, solidified into a light-brown cake, which, on crystallization from alcohol, gave small white needles. These were recrystallized from alcohol until they showed the constant melting-point 87° to 88°, when they were dried *in vacuo* and analyzed with the following results :

I. 0.1968 gram substance gave, on combustion, 0.2437 gram CO_2 and 0.0411 gram H_2O.

II. 0.1736 gram substance gave, by the Carius method, 0.2091 gram AgCl.

	Calculated for $C_6Cl_3(NO_2)_2CH_2COOC_2H_5$.	I.	Found. II.
C	33.58	33.76	....
H	1.96	2.33	....
Cl	29.80	....	29.79

[1] The nature of this body and its derivatives has not been determined with certainty. See the introduction to this paper.

The substance is therefore the trichlordinitrophenylacetic ester, but we are unable to determine whether it was formed during the action of the sodic malonic ester or the tetrachlordinitrobenzol, or, what seems more probable, during the distillation with steam by the partial saponification of the malonic ester, followed by the escape of carbonic dioxide.

Three grams of the trichlordinitrophenylacetic ester and 0.5 gram of trichlordinitrophenylmalonic ester were obtained from 5 grams of tetrachlordinitrobenzol, so that the yield was good.

Properties of Trichlordinitrophenylacetic Ester.—It crystallizes from alcohol in long, slender, branching, white needles with sharp ends, and melts at 87° to 88°. It is freely soluble in ether, benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide; slightly soluble in cold alcohol or ligroin, freely soluble in these solvents when hot; insoluble in water. Strong hydrochloric acid or strong nitric acid has no action on it, strong sulphuric acid dissolves it. Boiling dilute sulphuric acid saponifies it, giving trichlordinitrophenylacetic acid. It is decomposed with great difficulty by fuming nitric acid. Sodic hydrate has no apparent action on it.

Trichlordinitrophenylacetic Acid, $C_6Cl_3(NO_2)_2CH_2COOH$.— This acid was formed by the saponification of its ester. One gram of the trichlordinitrophenylacetic ester was boiled in a flask with a return-condenser with about 200 cc. of sulphuric acid of sp. gr. 1.44. This large proportion of the dilute sulphuric acid is necessary to ensure complete saponification. At first the substance melted and floated on the surface of the boiling acid, then a slight yellow color was developed, and after half an hour an effervescence began, which lasted thirty to forty minutes. After two hours the oily drops had disappeared, and small white needles began to crystallize out. The liquid was then allowed to cool, diluted with about three times its volume of cold water, the white crystals formed filtered out, and recrystallized from a mixture of benzol and ligroin until they showed the constant melting-point 190° to 191°, when they were dried at 100° and analyzed with the following results:

I. 0.1796 gram substance gave, by the Carius method, 0.2346 gram AgCl.

II. 0.2264 gram substance gave 17.4 cc. N_2 at 28° and 768 mm.

	Calculated for $C_6Cl_3(NO_2)_2CH_2COOH$.	Found. I.	II.
Cl	32.42	32.29	....
N	8.52	....	8.52

The yield was practically quantitative, and we are therefore unable to account for the effervescence observed during the saponification, which, at the time, we supposed was caused by the formation of a substituted toluol with the escape of carbonic dioxide.

Properties of the Trichlordinitrophenylacetic Acid.—It crystallizes from benzol and ligroin in white, well-formed prisms, probably belonging to the monoclinic system, which are usually broader than they are long, and terminated by a single plane at a very oblique angle to the sides. It was also obtained in long, slender prisms with blunt ends; and from benzol alone it crystallizes in rhombic plates, which probably contain benzol of crystallization, as they effloresce on exposure to the air. It melts at 190° to 191°, and is freely soluble in ethyl or methyl alcohol, ether, chloroform, or acetone; somewhat soluble in cold benzol, freely in hot; slightly soluble in carbonic disulphide; essentially insoluble in cold ligroin, soluble in it when hot; insoluble, or nearly so, in cold water, slightly soluble in hot. The three strong acids do not dissolve it when cold, but it dissolves in each when hot, more freely in nitric acid than in the other two. Warm sodic hydrate dissolves it, giving a yellow solution of the salt, but it is essentially insoluble in cold sodic hydrate. Even long boiling with alcohol did not convert it apparently either into the ester or the substituted toluol.

A yellow solution of the ammonium salt, prepared by dissolving the acid in warm ammonic hydrate and driving off the excess of ammonia on the water-bath, gave the following reactions:

Ferric chloride, a light-yellow precipitate ;
Plumbic acetate, a yellow precipitate ;
Argentic nitrate, a yellow precipitate.

With cupric sulphate there is no visible reaction at first,
but after standing a few minutes light-blue needles crystallize
out.   Cobaltous nitrate behaves in the same way except that
the needles are pink ; whereas, nickelous nitrate gives no
crystals even after standing fifteen minutes.   Baric chloride
gives no precipitate.

The silver salt was studied more carefully.   It is pale-yel-
low and insoluble in cold water.   Hot water dissolves a little
of the salt, which decomposes on boiling, giving a dark-col-
ored solution.   The air-dried salt, on the other hand, can be
dried at 100° without visible decomposition.   It is insoluble
in all the organic solvents except acetone, which gives a yel-
lowish-brown solution with it that turns black on boiling.

CAMBRIDGE, MASS., October, 1903.

THE ANALYSIS OF ORGANIC SUBSTANCES WITH THE HELP OF SODIUM PEROXIDE.

BY HANS H. PRINGSHEIM.

In a preliminary paper[1] I described a method for the quan-
titative determination of chlorine, bromine, and iodine as
found in organic substances.   In that article I promised to
extend my experiments for halogen determination to a greater
number of substances, and to find out whether the same
method of combustion could be used for the quantitative de-
termination of nitrogen.

I propose, in the present paper, to report upon all the ex-
periments up to date, as now the method for halogen deter-
mination has been fully worked out.

A short time ago M. Dietrich[2] reviewed the more recent at-
tempts to supersede the method of Carius and especially those
intended to establish a new one dispensing with the use of a
bomb-tube.   I have solved this problem with the help of

[1] Ber. d. chem. Ges., **36**, 4244 (1903).
[2] *Ibid.*, **36**, 3385-3387 (1903).

sodium peroxide. The proposed method has all the advantages necessary for an analytical method, as accuracy, general applicability, quickness, cheapness, and cleanliness.

Parr[1] shows that coal can be completely burned by first mixing it with sixteen to eighteen times its weight of sodium peroxide, and then starting the reaction by throwing a red-hot iron wire into the mixture.

For organic compounds, which contain different percentages of carbon and hydrogen, it is necessary to fix the proportion between the substance and the sodium peroxide so that, on the one hand, the violence of the reaction may be moderated, and, on the other hand, complete combustion may be effected. This result is reached when the heat evolved is strong enough to cause such a reaction through the whole mass that the reaction-residue will be completely melted. After experiments, therefore, I fixed the proportion between different substances and sodium peroxide as follows :

Substances with 75 per cent carbon and hydrogen need eighteen times their weight of sodium peroxide ; those having from 50 to 75 per cent carbon and hydrogen need sixteen times their weight of the peroxide. Substances containing 25 to 50 per cent carbon and hydrogen should be mixed with half their weight of a substance containing much carbon and hydrogen, such as sugar, naphthalene, cinnamic acid, etc. ; those with less than 25 per cent carbon and hydrogen should be mixed with their own weight of one of the substances above mentioned. To the mixture is then added, in the first case, sixteen times, in the second case, eighteen times its own weight of sodium peroxide.

In most cases, however, the work can be simplified and the weighing limited to the weighing of the substance only, if we take a greater amount of sodium peroxide than the experiment calls for (approximately twice the amount) and add to it the twenty-fifth part of its weight of carbohydrate. This mixture can be made up once for all ; the quantity of it to be used can be easily determined by filling the crucible up to a certain mark. This holds, when the substance does not come near to being all halogen or hydrocarbon.

[1] J. Am. Chem. Soc., **22**, 646.

Determination of Chlorine, Bromine, and Iodine in Solids.

The weighed substance, about 0.2 gram, is mixed with sodium peroxide in a steel crucible, of the form and size indicated in the accompanying illustration. The crucible is
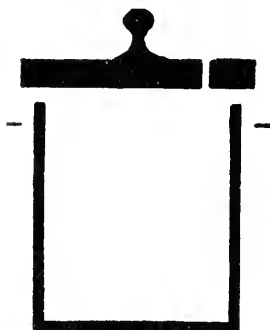
Fig. I.

placed in a porcelain dish, in which it is surrounded with water up to the marks, which appear in the illustration near to the lid. The combustion is then started by thrusting a red-hot iron wire into the mass through the hole in the lid. After allowing it to cool for a few minutes, the crucible is laid on its side in the water and the dish quickly covered with a watch-glass. The dish is then placed on the water-bath till the mass has completely dissolved, which result will have been reached when no more oxygen is given off. The crucible and lid are then removed, washed, and the alkaline solution and washwater filtered to remove any traces of carbon left from the combustion and any iron hydrate, which may appear in consequence of an oxidation of the wire or crucible.

In my previous paper I proposed to pour the filtrate into so much sulphurous acid that the alkali would be completely neutralized, and still enough sulphurous acid be left to reduce any halogen acids, or peracids, formed through too strong an oxidation, to hydroacids. This same end can, however, be reached, and the bulk of the liquid considerably reduced by adding to the filtrate about 5 cc. of a strong solution of sodium sulphite and acidifying with sulphuric acid. The sulphurous acid is thus freed, particularly on gently warming. To the solution is then added strong nitric acid and the halogen is precipitated with silver nitrate. The nitric acid keeps any silver sulphite, or sulphate, in solution. After standing on the water-bath till the precipitate has settled, the silver halide is filtered, best in a Gooch crucible over asbestos, and weighed in the usual way.

Iodoform, CHI_3.—0.1345 gram substance gave 0.2407 gram AgI.

Calculated.	Found.
96.62	96.69

p-Dibrombenzene, $C_6H_4Br_2$.—0.4875 gram substance gave 0.7779 gram AgBr.

Calculated.	Found.
67.79	67.90

Dibromsuccinic Acid, $C_4H_4O_4Br_2$.—0.3479 gram substance gave 0.4740 gram AgBr.

Calculated.	Found.
57.97	57.98

2,6-Dibrom-p-nitraniline, $C_6H_4O_2N_2Br_2$.—0.1072 gram substance gave 0.1355 gram AgBr.

Calculated.	Found.
54.05	53.79

p-Chlorpropanil, $C_9H_{10}ONCl$.—0.1931 gram substance gave 0.1512 gram AgCl.

Calculated.	Found.
19.35	19.36

Chloranil, $C_6O_2Cl_4$.—0.1136 gram substance gave 0.2645 gram AgCl.

Calculated.	Found.
57.73	57.57

Diethyl Dichlordinitrophenyimalonate, $C_{13}H_{12}O_8N_2Cl_2$.—0.2114 gram substance gave 0.1535 gram AgCl.

Calculated.	Fouud.
17.98	17.96

Tribromresorcinol, $C_6H_3O_2Br_3$.—0.2527 gram substance gave 0.4142 gram AgBr.

Calculated.	Found.
69.16	69.76

Dinitrobrombenzoic Acid, $C_7H_3O_6N_2Br$.—0.3962 gram substance gave 0.2585 gram AgBr.

Calculated.	Found.
27.49	27.76

Eosin, $C_{20}H_8O_5Br_4$.—0.2234 gram substance gave 0.2596 gram AgBr.

Calculated.	Found.
49.38	49.44

Tetrabrom-o-quinone, $C_6O_2Br_4$.—0.4147 gram substance gave 0.7368 gram AgBr.

Calculated.	Found.
75.46	75.61

Tetrabrompyrocatechin, $C_6H_2O_2Br_4$.—0.1301 gram substance gave 0.2305 gram AgBr.

Calculated.	Found.
75.12	75.39

Hexabromphenanthrene, $C_{14}H_4Br_6$.—0.0620 gram substance gave 0.1071 gram AgBr.

Calculated.	Found.
73.62	73.52

It will be seen from the foregoing list of results that, along with other substances, I have selected a number which are particularly hard to decompose in the bomb-tube.

Since all the compounds analyzed, which contain widely different groups and belong to the aliphatic as well as to the aromatic series, have given satisfactory results, I consider the method to be generally applicable.

Determination of Chlorine, Bromine, and Iodine in Liquids.

On attempting to use the same method for liquid as for solid substances, no correct results could be obtained at first. It was found that as an average of a considerable number of determinations, about one-sixth of the halogen was lost; the higher, or lower, boiling-point of the liquid had no marked influence on the result.

That a difference exists in the oxidizing power of sodium peroxide towards solids and liquids in an open crucible was finally proven in the following way :

p-Bromtoluene, melting at 28° C., was twice oxidized. The first time the temperature, up to the time of combustion, was kept just below its melting-point, with the following result :

p-Bromtoluene, C_7H_7Br.—0.3090 gram substance gave 0.3386 gram AgBr.

Calculated.	Found.
46.78	46.63

The second time, the temperature was kept just above the melting-point up to the time of combustion, with the following result :

0.3391 gram substance gave 0.3648 gram AgBr.

Calculated.	Found.
46.78	45.78

Since in both cases the substance was weighed as a solid, the loss in the second determination must be explained as due to incomplete oxidation of the liquid.

I then tried to cover the mixture of liquid and sodium peroxide with a layer containing only sodium peroxide and carbohydrate. But this did not improve the result, as, naturally, the top layer lost its oxidizing power before the liquid was reached.

To overcome the difficulty a closed crucible, of the form and size represented in the accompanying illustration, was constructed. The lid can be screwed on. It bears in its middle a perforation just big enough to hold a capillary glass tube, into which is melted a copper wire of suitable length, ending in its lower part in a loop. The glass tube is cemented into the lid with "de Khotinski cement." Under the lid is placed a ring of softer metal, large enough to stay in its place and to rest on the rim of the crucible. This will insure, on screwing, a tighter connection.

Fig. II.

Lead is too easily oxidized, but copper will serve the purpose sufficiently well. To the loop of the copper wire is fixed a
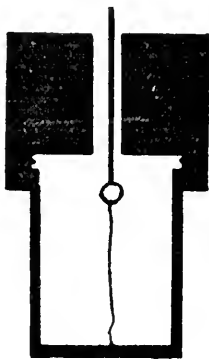
piece of fine picture wire, just long enough to touch the bottom of the crucible.

The amount of sodium peroxide demanded by the rule previously given, is now placed in the crucible. On it is poured the liquid to be analyzed, from a weighed pycnometer, which is protected against evaporation by pushing a ground glass cap over the side-tube, through which the liquid has to be poured. Ten drops of liquid will be about the desired weight. The substance and sodium peroxide are then quickly mixed with the help of a platinum wire, and the upper space in the crucible is filled with the sodium peroxide-carbohydrate mixture. The lid is screwed on, care being taken to run the fine wire through the middle of the crucible, so that it will touch the bottom.

If now the crucible is brought into connection with one pole of an electric battery, while the copper wire in the lid is connected with the other pole, the picture wire can be easily fused and the mass ignited inside of the closed crucible. If care is taken that a fuse wire has been provided, of such a thickness that it will offer less resistance than the picture wire, the direct current for electric lights can be used with convenience for this operation. It is necessary to have the crucible completely filled with sodium peroxide without, however, pressing it in. Only in this way can complete combustion of the liquid be obtained. As the carbonic acid and water formed during the reaction will be taken up by the sodium peroxide, and as nitrogen is not present in such a quantity as to create a considerable inside pressure, there is no danger of explosion connected with this operation. After cooling, the lid can be easily removed, the reaction-residue dissolved, and the halogen determined in the way described above.

Brombenzene, C_6H_5Br.—0.4060 gram substance gave 0.4829 gram AgBr.

Calculated.	Found.
50.95	50.61

o-Chlortoluene, C_7H_7Cl.—0.1564 gram substance gave 0.1798 gram AgCl.

Calculated.	Found.
28.06	28.43

Epichlorhydrin, C_3H_5OCl.—0.2132 gram substance gave 0.3279 gram AgCl.

Calculated.	Found.
38.38	38.03

Isobutyl Bromide, C_4H_9Br.—0.1680 gram substance gave 0.2289 gram AgBr.

Calculated.	Found.
58.39	57.98

Chloral Hydrate, $C_2H_3O_2Cl_3$, could be analyzed only in the closed crucible.

0.2045 gram substance gave 0.5300 gram AgCl.

Calculated.	Found.
64.35	64.09

Determination of Phosphorus and Arsenic in Organic Substances.

Although the number of organic substances, so far prepared, containing phosphorus or arsenic has not been great, this method for their quantitative determination must be considered a valuable addition, for no short method for this purpose has been in use hitherto.

For the determination of phosphorus and arsenic it is advisable to employ a somewhat larger proportion of sodium peroxide, about half the amount more in addition to that calculated for the halogen determination. It is better to oxidize the substance in a silver crucible, so as to avoid the introduction of iron, which would complicate the final determination of phosphorus and arsenic unnecessarily. For the same reason the reaction is better started by using a copper wire.

In the case of phosphorus the alkaline solution was acidified with hydrochloric acid and, after neutralizing with ammonia, was precipitated with magnesia mixture.

Guajacophospham, $P(C_6H_3(OH)OCH_3)_3$.—0.3692 gram substance gave 0.1023 gram $Mg_2P_2O_7$.

Calculated.	Found.
7.75	7.71

Diethylphosphoric Acid, $PC_4H_{11}O_4$.—0.0766 gram substance gave 0.0561 gram $Mg_2P_2O_7$.

Calculated.	Found.
20.13	20.39

In the case of arsenic the alkaline solution was twice evaporated with nitric acid to insure a complete oxidation of the arsenious to arsenic acid. This was the precipitated, washed, and weighed, following the method of Friedheim and Michaelis.[1]

Methylarsinic Acid, $AsCO_3H_5$.—0.1650 gram substance gave 0.1826 gram $Mg_2As_2O_7$.

Calculated.	Found.
53.57	53.42

Tritolylarsine, $C_{21}H_{21}As$.—0.2711 gram substance gave 0.1234 gram $Mg_2As_2O_7$.

Calculated.	Found.
21.55	21.97

Attempt at a Quantitative Determination of Nitrogen.

I thought of using the oxidizing power of sodium peroxide for a nitrogen determination, provided the peroxide would not be decomposed by dry carbon dioxide. This was found not to be the case. The substance to be analyzed was mixed with the sodium peroxide and the mixture put into a brass retort, connected on one side with a suitable arrangement for developing carbon dioxide, and on the other side through a T-tube, with a short combustion-tube, holding two reduced copper spirals of common length. This latter tube was further connected with the pipette used for nitrogen determination. After the apparatus had been completely filled with carbon dioxide the retort was closed off from the carbon dioxide generator and the pipette, and exhausted through the T-tube, to make room for the nitrogen which was then set free in the retort by starting the combustion through outside heat. The

[1] Ztschr. anal. Chem., **34**, 505.

vacuum not filled with the gases, produced in the retort, was then filled up with carbon dioxide and the gases driven over the copper spirals into the azotometer, where the volume was determined. The first spiral may be oxidized by some oxygen set free during the reaction, and the oxygen so separated from the nitrogen.

In my first experiment I found 9 per cent instead of 10.37 per cent nitrogen for acetanilide. As, on repetition, no higher results could be reached and, as the deficiency of nitrogen amounted to about 10 per cent in several cases, as, for instance, 17.5 per cent instead of 20.05 per cent for potassium ferrocyanide, 27 per cent instead of 31.82 per cent for oxamide, I finally looked for nitrous acid in the reaction-residue. By using a large amount of a substance containing a high percentage of nitrogen, nitrous acid was found to be present.

So far no way has suggested itself to me of avoiding this higher oxidation, or of reducing the sodium nitrite in a way short enough to make the method practicable.

Summing up the results, I venture to say that my method is well suited to supersede the Carius method for solids ; that it is available for the determination of phosphorus and arsenic ; that liquids may be analyzed in a shorter time than in a bomb-tube, and perhaps with no greater number of failures in results ; and that the attempt to determine nitrogen, with the help of sodium peroxide, though unsuccessful, has been an interesting experiment, and one which encourages me to further efforts.

I wish to express my thanks to Prof. C. Loring Jackson for his kind counsels in every stage of the progress of my investigation.

THE COMPOSITION OF DOUBLE HALOGEN SALTS.

BY H. L. WELLS.

Fritz Ephraim,[1] from observations made on double fluorides of vanadium, and from other considerations, believes that he has discovered some laws which are applicable to double

[1] Ber. d. chem. Ges., **36**, 1177, 1815, 1912.

halogen salts in general. It is his opinion that the number of molecules of positive metal halide which are capable of combining with a negative halide is greater :

    1. When the atomic weight of the positive metal is smaller.

    2. When the atomic weight of the negative metal is greater.

    3. When the atomic weight of the halogen is smaller.

These views have been criticized by Grossmann[1] and by Pfeiffer,[2] who maintain that the laws are not applicable in a general way. I will state here that I agree with the opinions of Grossmann and Pfeiffer, and without again taking up the points discussed by these authors, will make a few additional observations.

The first rule which Ephraim gives is not a new one, as far as it refers to certain series of compounds. Wells and Foote,[3] in connection with investigations on double fluorides of zirconium, noticed a rule which includes Ephraim's and applies also to the negative end of a series of salts. Their statement was as follows : '' The (alkaline) fluorides of smaller molecular weight gave types with a larger number of these molecules, while the fluorides with higher molecular weights combined with more zirconium fluoride than the others.''

Ephraim presents the following formulas in support of his view.

$$6NH_4F.V_2F_6 \qquad 5NaF.V_2F_6 \qquad 4KF.V_2F_6$$
$$9NH_4F.3VOF_2 \qquad 8NaF.3VOF_2 \qquad 7KF.3VOF_2$$
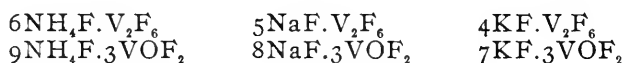
Wells and Foote gave the following series :

Type.	Lithium salts.	Potassium salts. Marignac.	Caesium salts.
4 : 1	$4LiF.ZrF_4.\frac{2}{3}H_2O$	. . . .	. . . .
3 : 1	. . . .	$3KF.ZrF_4$	. . . .
2 : 1	$2LiF.ZrF_4$	$2KF.ZrF_4$	$2CsF.ZrF_4$
1 : 1	. . . .	$KF.ZrF_4.H_2O$	$CsF.ZrF_4.H_2O$
2 : 3	. . . .	. . . .	$2CsF.3ZrF_4.2H_2O$

Wells and Foote found, however, that this rule did not apply to the sodium and thallium double fluorides of zirconium, which are as follows :

[1] *Ibid.*, **36**, 1600, 2499.
[2] *Ibid.*, **36**, 2519.
[3] Am. J. Sci., **3**, 466 (1897).

$$5\text{NaF}.2\text{ZrF}_4 \qquad 2\text{NaF}.\text{ZrF}_4$$

$$3\text{TlF}.\text{ZrF}_4 \qquad 5\text{TlF}.3\text{ZrF}_4 \qquad \begin{cases} \text{TlF}.\text{ZrF}_4 \\ \text{TlF}.\text{ZrF}_4.\text{H}_2\text{O} \end{cases}$$
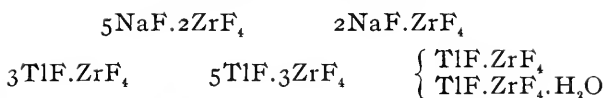
Therefore, the rule evidently has only very limited application, a point which was considered by the writer in an article[1] referred to by Ephraim, and with which, consequently, he should have been familiar.

In regard to Ephraim's second and third generalizations, it may be mentioned that the effects of varying atomic weights in connection with the more negative metal and the halogen have been carefully considered, as far as they seemed to apply to certain limited series of salts, long before the matter was taken up by Ephraim. Some remarks by Wells and Campbell[2] on this subject will be merely referred to here.

Another matter must be considered here. It is the rejection by Ephraim, without any experimental evidence, and merely because, from his point of view, they ought to be simpler, of the complicated 23 : 10 (or 7 : 3) alkaline-antimonious halides. Ephraim is here inconsistent in wishing these salts to be simpler, for he has given as an evidence of his first law a salt with exactly the same complex ratio, $7\text{KF}.3\text{VOF}_2$, which has been mentioned above. Moreover, he has overlooked the work of Wells and Foote[3] on one of these salts, $7\text{RbCl}.3\text{SbCl}_3$, where the investigators made every effort to find that the salt was a mixture. His opinion that these salts are impure 2 : 1 compounds is certainly without foundation, for $7\text{RbCl}.3\text{SbCl}_3$, at least, can be repeatedly recrystallized from hydrochloric acid solution without change in composition, whether the acid is concentrated or moderately dilute. In spite of the importance attached by Ephraim to the matter, it is certain that recrystallization from hydrochloric acid would be capable either of removing or increasing, to some extent, an impurity consisting of potassium or rubidium chloride from these double salts. Too much careful work[4] has

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[1] This JOURNAL, **26**, 389 (1901).

[2] Am. J. Sci., **46**, 431 (1893).

[3] *Ibid.*, **3**, 461 (1897).

[4] Some facts given by Jordis (Ber. d. chem. Ges., **36**, 2539) indicate that he has prepared the salt $7\text{KCl}.3\text{SbCl}_3$, but apparently he considers the product a mixture.

been done on these complex salts to admit of their composition being overthrown by the expression of a preference.

SHEFFIELD SCIENTIFIC SCHOOL,
NEW HAVEN, CONN., Jan., 1904.

ON THE ACTION OF DRY HYDROCHLORIC ACID GAS DISSOLVED IN ANHYDROUS BEN-ZENE ON DRY ZINC.

BY KAUFMAN G. FALK AND C. E. WATERS.

PART I.

BY KAUFMAN G. FALK.

In an article published in 1902,[1] Kahlenberg described a number of experiments which he claimed refuted the theory of electrolytic dissociation. Among other things, he tested the action of dry hydrochloric acid, dissolved in anhydrous benzene, on a number of metals. Zinc was most readily attacked, the evolution of hydrogen continuing until a coating of the chloride was formed. The solution of acid in benzene showed no conductivity, according to a method devised by Kahlenberg. It is evident from the description of the apparatus that moisture was not entirely excluded, as the flask containing the benzene was opened just before passing in the hydrochloric acid. Rubber stoppers were also used in several places. With the intention of using the hydrogen to reduce certain substances that are acted on by water, attempts were made by me to repeat this work. Although the gases were not dried as completely as in the work of Kahlenberg, since the tubes containing the pentoxide of phosphorus were smaller, our results were entirely different from his. One would expect that the action would be greater, with more moisture present, but it entirely ceased in a few minutes, instead of continuing for hours. A protective coating was evidently formed on the zinc, and when very small amounts of water were admitted the action began again.

These facts were incidentally mentioned at the Washington meeting of the American Chemical Society by President Remsen. Afterwards H. E. Patten, in connection with whose

[1] J. Phys. Chem., **6**, 1.

paper read at that meeting a discussion was started, offered to
repeat his work at this laboratory.   His results and the ac-
count of further work upon the subject have been published.[1]
I have repeated the experiments in the same form since the
article of Patten appeared, and have obtained additional data.
The fact that the protective coating stopped the action was
shown by shaking the flask, which removed it in part and al-
lowed the action to start again.   This is in accordance with
the statements of Patten.   On admitting water, however, the
layer is not dissolved, as he stated, but the acid in the pres-
ence of this water seems to be able to act through the layer
which is first formed, and continues to act until a second and
thicker one is produced.   Patten, after his visit to Baltimore,
performed an experiment that was the most careful one re-
corded up to date.   But, as he stated, the point most open to
criticism was the use of rubber connections, which should
have been avoided.   Under these conditions the zinc was
acted on as before.

We, therefore, decided to construct an apparatus that would
not be liable to adverse criticism on this account.   The essen-
tial features of it were devised by Dr. Frazer.   Hydrochloric
acid was generated in a balloon-flask by allowing concentra-
ted sulphuric acid to drop slowly upon ammonium chloride.
It was then passed through three wash-bottles containing con-
centrated sulphuric acid, then into a tube 20 cm. long and 2
cm. in diameter, containing alternate layers of phosphorus
pentoxide and glass wool.   From this it passed through a
second tube containing glass wool upon which pentoxide had
been deposited by distillation in a current of dry oxygen.
From the drying-tubes the gas passed into one arm of an in-
verted T-tube, the stem of which contained a small spiral of
the same zinc wire that had been used before, and which was
also used by Patten in some of his experiments.   To the stem
was attached a guard-tube with pentoxide and glass wool, and
then two Drechsel bottles partly filled with concentrated sul-
phuric acid.   To the other arm of the T-tube was attached the
inner tube of a condenser, at the upper end of which a second

[1] J. Phys. Chem., **7**, 153. See especially pages 179-189.

one was attached by fusing together the inner tubes. To the lower end of the second condenser was joined a flask resembling a distilling-flask with the side tube bent upward. The neck was made by fusing to it one side of a ∪-tube, with a glass stopper and side tube, such as is used in organic combustions. As air was to be admitted through this tube later, it was connected with two guard-tubes containing pentoxide. The flask was partly filled with benzene that had been shaken with sulphuric acid, washed with caustic soda, then with water, dried over calcium chloride, then frozen, the last portions being discarded, and allowed to stand over phosphorus pentoxide.

Two platinum plates were fused into the side of the tube containing the zinc by means of wires, the outer ends of which were joined to short pieces of tubing that acted as mercury cups for making electrical connection. The plates were about 1 x 3 cm. and were about 1 mm. apart, and were kept in position by a drop of glass at each end. They were covered with platinum black.

The only pieces of rubber in the apparatus were the stopper of the flask in which the hydrochloric acid was generated and a piece of tubing at the outer end of one of the guard-tubes containing phosphorus pentoxide.

The stoppers of the Drechsel bottles were lubricated by the mixture recommended by Travers.[1]

When everything was ready, thin slices of sodium were put into the flask containing the benzene, which was then boiled, the first condenser returning it to the flask. At the same time a slow current of air was passed through the apparatus, escaping through two different guard-tubes of phosphorus pentoxide, so as to sweep all moisture from the apparatus. The tube containing the zinc was heated in a cylindrical air-bath to 150° for six hours. After standing three days the tube and zinc were again heated for three hours in a current of air. The next day sufficient benzene to nearly fill the reaction-tube was distilled over from the flask. To prevent this being drawn back into the flask as it cooled, the stop-cock at the

[1] Study of Gases, p. 25.

upper end of the flask was opened, thus admitting air through the two guard-tubes of pentoxide. Hydrochloric acid was then passed into the benzene through the drying-train described above. Bubbles of a gas were evolved from the zinc, and continued steadily for over an hour. The bubbles of gas were very small, and the amount of gas produced was too slight to have been measured except after the lapse of a considerable time. After two hours the action had diminished considerably, while after three hours it had practically ceased. The zinc was then covered with a thin even coating of chloride.

After the action had continued for about an hour, an attempt was made to determine the conductivity by the usual Kohlrausch method. When the reaction-tube was opposed by a resistance of 45,000 ohms no minimum could be detected. Besides the hydrochloric acid in the solution there may have been some zinc chloride, so that the conductivity would have been equal to the sum of the conductivities of the acid and the chloride. This was evidently of the order of magnitude found by Kablukoff,[1] who, using platinum electrodes 5 cm. long and 1 cm. wide and 1 mm. apart, found that the solution of hydrochloric acid in benzene had a resistance of 120,000,000 ohms. In view of these facts no further attempts to measure the conductivity were made. The hydrochloric acid is evidently not ionized as in a water solution.

A certain amount of water in the benzene seems in some way to hasten the formation of the protective layer on the zinc, so that the action stops sooner than when less water is present.

PART II.

By C. E. Waters.

The results obtained by Mr. Falk appeared to be so inconclusive that it was determined to repeat his experiments, taking even greater precautions than before. The one point that seemed most open to adverse criticism was that the zinc was heated in a current of air in order to dry it. It would thus become covered with a film of oxide, which would form

[1] Ztschr. phys. Chem., **4**, 429.

water if acted upon even to the slightest extent by the acid. Accordingly, a slow current of carefully dried hydrogen was used instead of air. The apparatus was practically the same as that used in the experiments described in Part I. But instead of three, there were seven wash-bottles containing concentrated sulphuric acid, and the hydrogen was purified by passing it through a solution of potassium permanganate, and then through an alkaline solution of pyrogallol. After this it went through a bottle with sulphuric acid, and then swept out the air from a flask, provided with a dropping-funnel and a delivery-tube, in which the hydrochloric acid was to be generated. From the flask it went through six wash-bottles fused together. Thence it was passed through tubes containing phosphorus pentoxide, etc., as in the experiments of Falk. The hydrogen was supplied from a Kipp apparatus provided at the top with a rubber stopper and a five-foot tube, of 1.5 cm. bore, in order to obtain the necessary pressure to force the gas through all the bottles of acid. By means of a pinch-cock the flow was so regulated that only ten or twelve bubbles passed per minute. The gas was allowed to flow all night, and the next day the tube containing the zinc was heated in the air-bath to a temperature of 300°–320° C. for eight hours. On the following morning, the benzene which had been standing over sodium, and then boiled with it as described by Falk, was distilled over into the tube containing the zinc. Then concentrated sulphuric acid was allowed to drop slowly from a long-stemmed dropping-funnel upon ammonium chloride, thus causing a slow current of hydrochloric acid to pass through the apparatus. When the benzene became well saturated with the gas there was evidently some action on the zinc, though even less than in the experiments of Falk. This continued for two or three hours, when the surface of the zinc was dark and slightly corroded. In our experiments the substances were plainly more carefully dehydrated than before, and there was less action, so that it appeared probable that there would be none at all if all the moisture were removed.

At the suggestion of Dr. Frazer, an apparatus was con-

From train of gas-bottles.

From hydrogen generator.

To 3 gas-bottles.
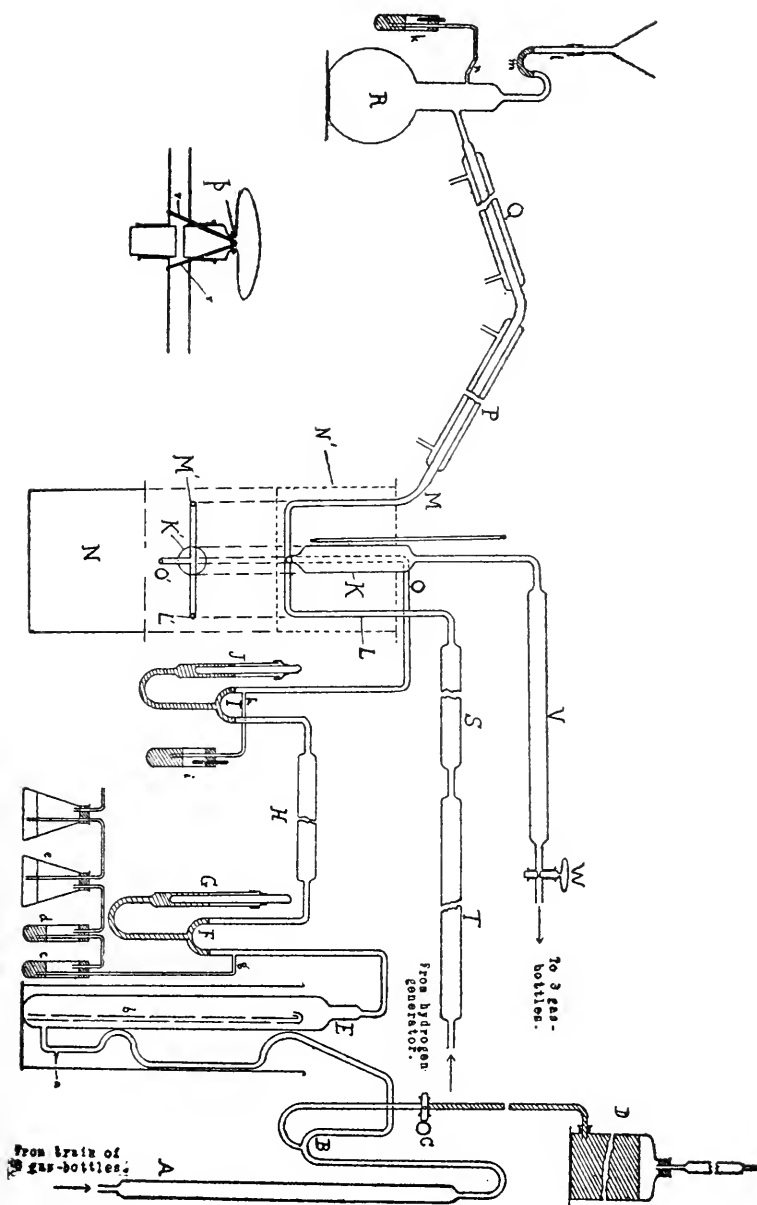
structed in which the hydrochloric acid gas could be kept in contact with the phosphorus pentoxide as long as desired. A description of the apparatus and the method of procedure follows: Hydrochloric acid was generated in a wide-mouthed bottle by allowing concentrated sulphuric acid to drip slowly upon ammonium chloride. A three-way stop-cock was introduced into one hole of the rubber stopper in order to pass the gas through the apparatus or to reduce the pressure rapidly, if desired, without permitting any back-flow of liquid from the drying-bottles. From this bottle the gas went through three Drechsel bottles fused together and containing sulphuric acid. It then went through a tube, A, 800 mm. long and 20 mm. bore, containing layers of phosphorus pentoxide and glass wool. At first the gas was allowed to pass out through D so as to sweep out the tube above the stop-cock C, after which it was sent through E, which was filled with pentoxide and glass wool. Before being filled with the drying agents, this tube was drawn out somewhat at the top so as to admit less moisture when the small tube was finally sealed to it. The mercury trap, F, being closed, the gas escaped through the lateral tube, g, under the mercury in c, which contained also a little pentoxide, then into d with sulphuric acid, and finally into water in the flasks e and f. These were so arranged as to prevent the water from sucking back into the acid.[1] When the air was driven from E mercury was run into B from D, and in this way the hydrochloric acid could be kept in contact with the pentoxide as long as desired. The tube G was then fused off.

The mercury trap, F, was made without the use of a bulb and long rubber tube, so as to avoid any diffusion of moisture into the apparatus. The tube, G, contained a piston, the outside diameter of which was about 4 mm. less than the bore of the tube, and was held air-tight by means of a short piece of rubber tubing fitted over both glass tubes. When the piston was not in the mercury the surface of the latter was just below the curve of F. By pushing the piston down, and at the same time slightly loosening the rubber, the mercury

[1] Lassar-Cohn: Arbeitsmethoden, 3rd. Edition, p. 311.

could be brought to any desired level in *F*, and to the same height in *G* by simple displacement. In this way there could be no tendency for the mercury to shift its level, as was seen to be the case when it stood higher in one tube than in the other. A little pentoxide was placed on the surface of the mercury in *G*, and all the mercury that was used here and throughout the apparatus was dried by shaking with pentoxide. The trap *I* was similar to *F*.

The tube, *H*, contained phosphorus pentoxide that had been distilled in a current of dry air and deposited upon glass wool previously placed in it. It was shut off from the rest of the apparatus by the traps, *F* and *I*. Further mention will be made of it later. While the hydrochloric acid was being passed through one part of the apparatus, the air was being driven from the rest of it by means of a slow current of hydrogen from a Kipp's apparatus, as already described. From the bottles containing potassium permanganate and pyrogallol it passed through six bottles of concentrated sulphuric acid into the tube, *T*, containing phosphorus pentoxide, and then through a second one, *S*, with redistilled pentoxide. Thence it passed through *L* into *K*, *O*, or *M*, as desired. In order to lose as little time as possible in driving the air out, the current of hydrogen was started one afternoon and allowed to run slowly all night, the cock, *W*, being open. In the morning it was closed and the hydrogen sent through *M* to drive out the air from the flask and condensers, and finally through *O* and out by way of *i*. The flow through the last two tubes was regulated by means of the glass plugs in the stoppers of the tubes containing mercury. At all times the current of gas was very slow. To drive the air from *R*, the benzene was kept boiling gently, and in this way the vapors filled the tube up to *n*, and the air above it would escape by diffusing into the hydrogen. When it was safe to heat the tube, *K*, a cylindrical air-bath, *N*, sheathed with asbestos, was placed under it on a tripod. The tube was kept at a high temperature. Preliminary experiments showed that when zinc dust is dried in a current of air at 365°–398° for two hours and then heated in a current of dry hydrogen at 355°, it gives up con

siderable moisture. From this it is believed that any zinc oxide that might be on the surface of the zinc would be reduced before the hydrochloric acid and benzene came in contact with it.

Of course the benzene was introduced before the current of hydrogen was started. A funnel was attached to the end of l by a rubber tube, and the benzene, which had been dehydrated, as already stated, was mixed with fresh pentoxide and poured in. The bend of the tube was then washed with a little pure benzene and enough mercury to close the bend was poured in. The outer end was then dried inside with a bit of paper and the tube sealed off with a small flame. In this way no moisture was admitted from the flame, and there was no danger of an explosion from the benzene vapor and air when it was sealed off.

When the hydrochloric acid had stood long enough in contact with the pentoxide in E, steam was run into the jacket of Q and at the same time the benzene was heated to boiling by means of a hot water-bath. A little more than enough to cover the zinc was distilled over. The water-bath was then cooled somewhat, but still kept under R to prevent the benzene from being drawn back again into the flask. Then the cock, C, was opened to admit some mercury, so that the gas in E was under a slightly greater pressure than in the tubes H and K. The traps, F and I, were then opened by raising the pistons. More mercury was then run into E so as to drive the gas slowly through H, which contained redistilled pentoxide, into the benzene in K. In order to prevent any possible stoppage of the mercury, the tube, b, with holes every inch or two, was placed in E, the idea being that the mercury could find its way up through this past any obstacle. The top was bent over to prevent its being clogged with pentoxide when E was filled.

The results of some experiments are given :

1. Some zinc was distilled under diminished pressure in an atmosphere of dry nitrogen, practically according to the method of Morse and Burton.[1] A small rod of it was filed into

[1] This JOURNAL, **10**, 312 (1888).

shape and smoothed with sandpaper. It was placed in K with a spiral of the same wire that was used in the previous experiments. They were kept from touching one another by placing the rod in a bit of glass tube open at each end. The wire was evidently impure, for it was acted on readily by dilute aqueous hydrochloric acid, giving at first a considerable residue that afterward dissolved. The sulphide was of a dirty yellowish-white. The distilled zinc was made from a specimen purer at first than the wire, and it was acted on only very slowly by aqueous hydrochloric acid. The sulphide was pure white. When a piece of filter-paper moistened with silver nitrate solution was held in the escaping hydrogen it was seen that both specimens of zinc contained arsenic. The wire contained more than commercial granulated zinc, while it took several minutes for the dark spot to appear when the distilled zinc was used.

The zinc was heated to 375° for two hours, and then to 355° for three hours. The hydrochloric acid was allowed to stand in contact with the pentoxide in E for twenty-four hours. When it was passed into K a tiny leak was noticed at the end of H nearest F, but nevertheless the experiment was continued to test the apparatus. There was evidence of exceedingly slight action on the wire, and what was surprising, a little more hydrogen came from the pure zinc. It was estimated that the gas was given off as rapidly as in the last experiments of Falk, but at no time could the action be called violent or rapid. The bubbles continued to appear for perhaps an hour.

2. The apparatus was then taken apart, cleaned, dried, and reconstructed. Fresh pieces of zinc were used, and were heated for five hours to 365° to 398°. The hydrochloric acid was kept in contact with the pentoxide in E for twenty-four hours. By the time the presence of hydrochloric acid could be detected at W, which was loosened for a moment, it was seen that bubbles were being given off from the surface of the piece of redistilled zinc in K. They seemed to come off from definite spots, and not from the entire surface. This continued for more than an hour. At no time was there any evidence to show that the coil of impure wire was being acted

upon. Not a single bubble was seen to come from its surface. The fact that it was enclosed in a tube slightly contracted at the lower end could have nothing to do with this, for nearly every bubble of hydrochloric acid passed through the tube, and there was free circulation of the liquid in all parts of K.

The way in which the hydrogen came from definite spots on the pure zinc seemed to indicate impurities giving an electrical couple, perhaps iron from the file with which the stick was shaped, though the surface was afterwards cleaned with sandpaper and filter-paper wet with benzene in the same way as the wire. It may be that particles of iron lodged in the crevices between the crystals of the zinc. Another thing that may have been a disturbing factor was that part of the surface of the zinc was much darkened after the heating, and the rest of it seemed to be clouded, instead of bright. Perhaps this was due to a deposit of carbon. An acid solution of permanganate gives off oxygen slowly, and this would tend to produce carbon monoxide when it was passed into the pyrogallol. It might easily happen that the monoxide would be reduced to carbon on the surface of the zinc when heated to 398° in hydrogen. When the apparatus was taken apart for cleaning, it was noticed that the dark deposit was nearly all removed by water. The few bits that remained could be rubbed off with ease. This is what we should expect if it were a superficial deposit of carbon.

3. The experiment was again repeated, removing the oxygen this time by means of copper. Copper powder was made by sifting zinc dust into a hot solution of copper sulphate, washing the precipitated copper with alcohol, then mixing it, while still moist, with short-fibred asbestos, washing with ether, and drying in a desiccator. The material was then placed in a tube of hard glass closely wound with copper gauze to prevent its bursting, when heated red-hot, under the pressure of the hydrogen. Instead of filing down a large stick of the redistilled zinc, a clean piece of it was melted in an atmosphere of nitrogen at reduced pressure, in a piece of Jena tubing closed at the lower end and drawn out to a tube of

about 4 mm. bore. In this way a slender rod of it was obtained that could be cleaned with sandpaper. With it were introduced a piece of the same wire that was used in the previous experiments, and a second piece of the wire with a little platinum wire wrapped around the middle. These were kept from touching one another by being placed in short pieces of glass tubing. To keep the pieces of zinc from falling out of the tubes, a sort of grating was formed at the bottom of each by drawing threads of melted glass rod across the opening.

When the apparatus was set up the copper was first reduced in a current of hydrogen, the water which was formed being allowed to escape at one end of a T-tube, which was closed when it was desired to pass the hydrogen through the apparatus. It is evident that all the oyxgen, which could be present only in small amount, would be burned to water in contact with the red-hot copper and hydrogen. '

After the benzene was distilled over into K, in this experiment, it was heated just to its boiling-point by means of the air-bath. This was done at the suggestion of Professor Morse, in order to remove the surface film of hydrogen upon the zinc.

The hydrochloric acid was kept in E for nine days. When it was passed into the benzene there was action on all the pieces of zinc. The rod of the distilled zinc and the wire seemed to give off equal amounts of hydrogen, while the wire with the platinum wrapped around it was apparently acted on least, though this may not have been due to its smaller surface. The action was greater than in the experiments preceding, though it was still exceedingly slow, and it ceased entirely within an hour. The zinc was slightly darkened and none of the white coating noticed by Patten was seen.

According to some rough determinations, benzene dissolves about two per cent of hydrochloric acid, by weight, at 18° C.

Various devices suggested themselves in connection with the working of the apparatus. To empty E with least risk, a small tube, a, was fused to the tube through which the mercury entered. At the proper time its point was broken off with a long rod, and the mercury flowed quietly into the cyl-

inder. In wiring in stopcocks there is no middle ground, they are either too tight or too loose. If rubber bands are simply twisted around them, the cock is apt to turn at the wrong time. Accordingly a piece of wire, *p*, was fastened to the cock so as to make a loose collar with two projecting hooks on opposite sides. The rubber band was then slipped over these hooks, and the cock could be set at any point and left without fear of its moving back. A similar device was used on the Drechsel bottles to keep the stoppers in place in spite of the pressure inside. Two strong bands were used on each bottle. The bottles were placed on little tables, made by nailing together three pieces of half-inch boards, six inches square, so that it was not necessary to cut them apart to clean and refill them. By slipping out the table the bottle could be removed from the stopper.

The admission of some moisture in sealing the joints of the apparatus is unavoidable. The amount thus introduced is lessened by keeping the ends of the tubes to be joined close together while being heated. In blowing into the apparatus to perfect the joint, a tube containing phosphorus pentoxide was always between the mouth and the apparatus.

Many useful suggestions were received from different workers in the laboratory, especially from Dr. J. C. W. Frazer.

Johns Hopkins Univ.,
    December, 1903.

RECENT RESEARCH ON RADIOACTIVITY.[1]

By P. Curie.

Since the discovery of strongly radioactive substances, research on radioactivity has been greatly developed. I propose in this article to give an account of the actual state of our knowledge relative to this subject, laying particular stress on the most recent work.[2]

I. Radioactive Substances.

Becquerel Rays. Uranium and Thorium.—We call radio-active such substances as are capable of emitting spontaneously and continuously certain rays known as Becquerel rays. These rays act upon the photographic plate ; they render the gases through which they pass conductors of electricity ; they can pass through black paper and metals. The Becquerel rays cannot be reflected, refracted or polarized.

In 1896 Becquerel discovered that uranium and its compounds emit these new rays continuously. Schmidt and Mme. Curie then found almost simultaneously that thorium compounds are also radioactive. The radiations emitted by thorium compounds are comparable in intensity with those from the compounds of uranium. Radioactivity is an atomic property that accompanies the atoms of uranium and thorium wherever they are found ; in a compound or a mixture its intensity is proportional to the amount of the metal present.

New Radioactive Substances.—Mme. Curie, in 1898, tried to learn whether there were among the elements then known any others possessing radioactivity ; she could not find a single substance giving any considerable radiation, and concluded that the radioactive properties of the elements are at least 100 times more feeble than those of uranium and thorium. She found, on the other hand, that certain minerals containing uranium (pitchblende, chalcolite, and carnotite) are more active than metallic uranium ; the activity of these minerals could not, then, be due solely to uranium or to other known elements. This discovery was fertile with new results. Mme. Curie and I showed, in an investigation carried on together, that pitchblende contains new radioactive substances, and we supposed that these substances contained new chemical elements.

There are known with certainty three new strongly radio-active substances : polonium, which was found in the bismuth obtained from the uranium minerals ; radium, found with barium from the same source, and actinium, which was dis-

covered by Debierne among the rare earths extracted from the same minerals. These three substances are present only in infinitesimal quantities in the uranium minerals, and all three possess a radioactivity about a million times greater than that of uranium or thorium.

Recently Giesel and Hofmann announced the presence of a fourth strongly radioactive substance in the uranium minerals, which had properties closely resembling those of lead; from the publications that have appeared up to this time I have not been able to form an opinion as to the nature of this substance.

It may be asked whether radioactivity is a general property of matter. This question cannot be regarded as actually settled. The investigations of Mme. Curie have proved that the different known substances do not possess an atomic radioactivity one-hundredth as great as that of uranium or thorium. On the other hand, certain chemical reactions may cause the formation of ions, conductors of electricity, without the active substance giving any evidence of atomic radioactivity. Thus white phosphorus by its oxidation renders the surrounding air a conductor of electricity, while red phosphorus and the phosphates are not at all radioactive.

Some old experiments by Russell, Colson and Lengyel showed that certain substances act upon the photographic plate at a distance. It is possible that this phenomenon is partly due to radioactivity, but it is not certain. Recent work by MacLennan and Burton, Strutt, and Lester Cooke, leads to the supposition that radioactivity belongs to all bodies to an extremely slight extent. The identity of these very feeble phenomena with atomic radioactivity can not yet be regarded as proved.

Radium.—Of all the strongly radioactive substances radium is the only one that has been proved to be a new element. Radium possesses a characteristic spectrum, the discovery and first study of which we owe to Demarçay, and which has since been studied by Runge and Precht and by Crookes. Radium is an element belonging after barium in the series of

alkaline earths. Its atomic weight as determined by Mme. Curie is 225.

At present radium is obtained from a residue left on extracting uranium from pitchblende. This residue contains 2 or 3 decigrams of radium in a ton. At first 10 or 15 kilograms of radiferous barium salt are extracted from a ton of the residue, and from this the radium is prepared by fractional crystallization (with the chloride or bromide), the crystals that form from the solution being richer in radium than the salt that remains in the liquid.

The radiant activity of the radium salt can be measured at different times from the beginning of crystallization until it is finally dried in the air-bath. It is found that the activity has a certain initial value, then it increases as a function of the time, at first rapidly, then more and more slowly ; it approaches asymptotically a limiting value which is about five times as great as the initial activity. The activity then remains invariable for some years if the salt be left as it is.

Polonium.—Polonium is, on the contrary, a substance that slowly loses its radioactivity from the moment when it is separated from the uranium mineral containing it. After some years the radioactivity of polonium almost completely disappears. Hence it acts like an unstable substance. It has not yet been shown that polonium is a new element distinct from ordinary bismuth.

Polonium can be concentrated by fractionally precipitating the subnitrate of polonium and bismuth by means of water. The part precipitated is the most active. One can also make a partial precipitation by means of hydrogen sulphide from a strongly acid solution in hydrochloric acid. These methods of fractionation are difficult because the precipitates are not easily redissolved. Marckwald concentrated the activity by plunging a rod of bismuth in a solution of bismuth and polonium. A layer of extremely active metal was deposited upon the rod.

Actinium.—The concentration of actinium is even more difficult than that of polonium. Solid salts containing actinium preserve their radioactivity unchanged for several years.

II. *The Radiations from Radioactive Substances.*

Complexity of the Radiation.—Radium is the substance whose radioactivity has been studied most completely. It is now known that it emits a number of rays of different nature, which can be placed in three groups. According to the notation adopted by Rutherford, I designate the three groups of rays by the letters α, β, and γ.

The action of the magnetic field serves to distinguish them. In an intense magnetic field the α-rays are slightly deviated from a straight path, and the deviation is of the same kind as that of the "canal" rays of Goldstein in a vacuum-tube. On the other hand, the β-rays are deviated like the cathode rays, and the γ-rays are not turned aside, but act like the Roentgen rays.

β-Rays.—The β-rays of radium, analogous to the cathode rays, form a heterogeneous group. They are distinguished from one another by their power of penetration and by the deviation caused by a magnetic field.

Certain β-rays are absorbed by aluminium foil a few hundreths of a millimeter in thickness, while others pass through several millimeters of lead.

Suppose we have a rectilinear pencil of Becquerel rays obtained by means of a particle of radium salt and a screen with a hole in it. If a uniform magnetic field is produced normal to the direction of the pencil the β-rays are incurved, and describe circular paths in a plane normal to the direction of the magnetic field. The rays of the described circumferences vary within wide limits. Becquerel has shown that the most penetrating rays are least deviated, and hence describe circumferences with the greatest radius of curvature. If the pencil of β-rays bent aside by the magnetic field is allowed to fall on the photographic plate, there is obtained an impression that is a true spectrum in which the different β-rays act separately.

Suppose the β-rays to be projectiles (electrons) negatively charged with electricity and shot from the radium with great velocity. Let m be the mass of a projectile, e its charge, v

its initial velocity, ρ the radius of curvature of its path, H the intensity of the magnetic field normal to the initial velocity, μ the magnetic permeability of the medium. We then have the easily established relation

$$(1) \qquad \mu H \rho = \frac{mv}{e}.$$

The β-rays are also deviated in an electric field. Suppose we have a rectilinear pencil of these rays. If a uniform electric field be produced normal to the initial direction of the pencil, the rays are deviated in the opposite direction to the field, and describe parabolic paths. The experiment can be performed by passing the pencil of rays between two parallel metallic plates, between which there is established a difference of potential. The deviation is slight with the means one has at command, and it is convenient to work in a vacuum. The air is made a conductor of electricity, so that if we work in the air the insulation is imperfect, and it is difficult to maintain a constant and high difference of potential between the plates. The most penetrating β-rays are bent aside least.

The action of the electric field is in accord with the ballistic hypothesis previously stated. Accepting this hypothesis, suppose a uniform electric field with an intensity h and a width L acts upon the charged projectile whose initial velocity is normal to the field. The deviation, y, of the extremity of the trajectory at the departure from the field is given by formula (2), when the deviation is slight.

$$(2) \qquad \frac{hL^2}{2y} = \frac{mv^2}{e}.$$

From the equations (1) and (2) can be deduced the velocity, v, of the projectiles, and the ratio, $\dfrac{e}{m}$, of the electric charge to the corresponding mass.

The experiments of Becquerel have shown that for the β-rays of greatest intensity the ratio, $\dfrac{e}{m}$, approaches 10^7

electromagnetic units, and v a value of $1.6 \times 10^{10} \dfrac{cm}{sec}$. These values are of the same order of magnitude as for the cathode rays.

Kaufmann has made exact experiments on the same subject. This physicist subjected a very narrow pencil of radium rays to the simultaneous action of a magnetic and an electric field, both fields being uniform and acting normal to the primary direction of the pencil. The pencil is received upon a photographic plate placed perpendicular to its initial direction. In the absence of the two fields the impression on the plate is a small circular disk, almost like a point. When the magnetic field acts alone the different β-rays are unequally deflected but remain in a plane normal to the field, producing upon the plate an impression in the form of a straight line. When the electric field acts alone the different β-rays are unequally deflected in a plane passing through the field and producing upon the plate an impression which is a straight line perpendicular to the one preceding. When both fields act simultaneously the impression on the plate is a curve. Each point of the curve corresponds to a different kind of β-ray. Taking as axes of coordinates on the plate the straight lines obtained when each of the two fields acts alone, the coordinates of each point of the curve represent the relative magnetic and electric deviations for each kind of ray.

The following are the figures for v and $\dfrac{e}{m}$ obtained by Kaufmann, referred to the most penetrating rays of radium. I give for comparison the values obtained by Simon for the cathode rays.

$\dfrac{e}{m}$ in electromagnetic units.	$v \dfrac{cm}{sec}$.	
1.865×10^7	0.7×10^{10}	(For the cathode rays. Simon.)
1.31×10^7	2.36×10^{10}	
1.17×10^7	2.48×10^{10}	(For the radium
0.97×10^7	2.59×10^{10}	rays. Kauf-
0.77×10^7	2.72×10^{10}	mann.)
0.63×10^7	2.83×10^{10}	

It is seen that certain β-rays have a velocity approaching that of light. One can understand why it is that particles having such velocity should be able to penetrate matter to such an extent, although they are so small.

The ratio $\frac{e}{m}$, seems to be the same for the least penetrating radium rays and the cathode rays. But this ratio dimishes as the velocity of the rays increases. J. J. Thomson and Townsend think that all charged electrons, when in motion, possess the same charge, which is equal to that carried by an atom of hydrogen when a solution is electrolyzed. If that be true, it must be admitted that the mass of the particles increases with their velocity, when the latter approaches that of light.

In the case of electrolysis the ratio, $\frac{e}{m}$, is equal to 9650, while this same ratio is equal to 1.865×10^7 for the cathode rays and the less penetrating β-rays. If it be admitted that the charge, e, is the same in both cases, it can be deduced that the mass of an electron is about two thousand times less than that of an atom of hydrogen.

Theoretical considerations lead to the conception that the inertia of a particle is solely due to its being a moving charge, the velocity of a moving electric charge not being altered without some change of energy. In other words, the mass of the charged particle is, in part at least, an apparent mass or an electromagnetic mass. Abraham gave a formula for calculating the electromagnetic mass of a charged particle as a function of its velocity. According to this formula the mass due to electromagnetic reactions is a constant for low velocities ; it increases with the velocity, and approaches infinity for velocities that approach that of light. The experiments of Kaufmann are in accord with this theory, and also lead to the conclusion that the mass of an electron is entirely of an electromagnetic nature. These results are of great theoretical importance. One can foresee the possibility of establishing mechanics upon the dynamics of small material centers charged and in motion.

α-Rays.—The α-rays of radium have very little power of penetration. A piece of aluminium foil a few hundredths of a millimeter in thickness absorbs them almost completely. They are also absorbed by the air, and cannot penetrate air at the atmospheric pressure to a greater distance than 10 cm. The α-rays form the most important part of the radiation of radium, provided we measure the radiation by the amount of ionization which it produces in the air.

The α-rays are very slightly deflected by the most intense magnetic and electric fields, and they were at first thought to be non-deviable under this influence. Nevertheless, independently of the action of the magnetic field, the laws of the absorption of the α-rays by superimposed screens is sufficient to distinguish them clearly from the Roentgen rays. In passing through successive screens the rays become less and less penetrating, while the penetrating power of the Roentgen rays increases. The ray is like a projectile whose energy diminishes on passing through each screen. A given screen also absorbs the α-rays to a much greater extent when it is placed at a distance than when it is placed quite near the radium.

Strutt suggested that the rays might be analogous to the canal rays of vacuum-tubes. Rutherford succeeded in showing the action of a magnetic field upon the rays and in making a preliminary measurement of the deviation. Becquerel confirmed the results obtained by Rutherford and gave a new measurement of the phenomenon. Des Coudres measured the electrical and magnetic deviation of the rays in a vacuum.

From these investigations it is seen that the α-rays act like projectiles having a great velocity and charged with electricity. The deviation in a magnetic field and in an electric field is the opposite of the deviation of the cathode rays.

The α-rays form an apparently homogeneous group, all being deflected to the same extent and, hence, not giving a spread-out spectrum as the rays do. The formulas (1) and (2) are applicable. According to the measurements of des Coudres in a vacuum,

$$v = 1.65 \times 10^9 \quad \text{and} \quad \frac{e}{m} = 6400.$$

Hence the velocity of the particles is twenty times less than that of light. If we assume that the charge of a particle is the same as that of an atom of hydrogen, in electrolysis, it is found that its mass is of the same order of magnitude as the hydrogen atom (the ratio, $\frac{e}{m}$, is equal to 9650 for hydrogen in electrolysis). It may well be supposed that these particles, which are greater than the electrons and have a lower velocity, would be less capable of penetration.

According to the experiments of Becquerel, the curvature of the path of the α-rays moving in a uniform magnetic field is not constant when in air at the atmospheric pressure. At first the curvature is the same as that obtained in a vacuum, but it becomes less and less as the ray recedes from its source. This phenomenon can be explained by supposing that new particles attach themselves to the projectiles that make up the rays while the latter move through the air. This hypothesis explains why the absorbing power of a screen for the α-rays increases as it is removed farther from the radiant source.

The α-rays are the ones that are active in the very beautiful experiments with the spinthariscope of Crookes. In this apparatus a very small fragment of a salt of radium (a fraction of a milligram) is held by a metallic thread a short distance (0.5 mm.) from a phosphorescent screen of zinc sulphide. On examining, in the dark, the surface of the screen which is toward the radium by means of a magnifying glass, luminous points are seen sprinkled over the screen, reminding one of a starry sky. These luminous points appear and disappear continuously. From the ballistic theory it might be imagined that each luminous point that appeared and disappeared resulted from the shock of a projectile. This is the first instance of a phenomenon which enables one to distinguish the individual action of an atom.

γ-*Rays.*—The rays are exactly like the Roentgen rays. They seem to comprise but a small part of the total radiation. The γ-rays have a very extraordinary power of penetration, and they diffuse very little in passing through most substances.

Diffusion of the Radium Rays.—Suppose we have a pencil of Becquerel rays issuing from radium and limited by a screen of lead. If the pencil meets a thin screen the α-rays are absorbed, the β-rays are diffused in all directions, and the γ-rays go part way through the screen as a well-defined pencil with sharp edges. The γ-rays can also pass through a prism of thick glass as a well-defined straight pencil. The question has been raised whether the β-rays are always completely diffused when they penetrate a solid screen. The experiments of Becquerel show that a pencil of β-rays can propagate itself in a well defined way in paraffin. Becquerel made use of the action of the β-rays on the photographic plate to study the path of the rays when dispersed by a magnetic field. It can be seen from the prints that the most penetrating rays pass through 7 or 8 mm. of paraffin without marked diffusion, while the least penetrating rays are completely diffused after passing through 2 mm. The magnetic field deflects the β-rays in paraffin as in air.

Conductivity of Dielectric Liquids under the Influence of the Radium Rays.—Dielectric liquids become poor conductors under the influence of the radium rays. This can be shown with petroleum, ether, vaseline oil, benzene, amylene, carbon disulphide, and liquid air.

Radiation of Other Radioactive Substances.—Polonium emits only very slightly penetrating rays, which seem to be identical with the α-rays of radium. They possess almost the same power of penetration and are deflected in the same way by the magnetic field. Finally, the experiment of the spinthariscope can be performed with the α-rays of polonium. Hence, polonium is a source of the α-rays unmixed with other kinds of rays, which is of value in certain studies. But the source exhausts itself, and some years after it has been separated from the minerals containing it the polonium loses its activity.

Thorium, uranium, and actinium seem to emit the α- and β-rays; the deviability of the β-rays has been shown.

The Electric Charge of the Radium Rays.—According to the

ballistic theory, the α-rays should carry positive electric charges and the β-rays negative electric charges. Mme. Curie and I have shown that, in conformity to the theory, the β-rays of radium charge positively the bodies that absorb them. To show this, a plate of lead is connected with an electrometer. The plate of lead is entirely covered with a layer of paraffin, which is in turn enveloped in fine aluminium foil connected with the earth. The radium, placed in a small dish, sends its rays upon the plate of lead, which is thus protected. The α-rays are stopped by the exterior layer of aluminium. Part of the β-rays pass through the aluminium and the paraffin and are absorbed by the lead, which becomes charged negatively. The paraffin is necessary to sufficiently insulate the plate of lead, which could be charged if it were surrounded by air, for it is made a conductor by Becquerel rays.

We have also shown that a salt of radium is charged positively when it is enveloped in an insulating layer, and that it emits β-rays from the exterior, while the α-rays cannot escape.

A sealed glass bulb containing a salt of radium becomes spontaneously charged like a Leyden jar. If after a sufficient time a mark is made on the wall of the flask with a glass-cutter, a spark is discharged, which pierces the glass at the point where it was made thin by the cutter. At the same time the experimenter feels a slight shock in his fingers from the passage of the discharge.

Phosphorescence of Substances under the Action of the Becquerel Rays. Light Emitted by Salts of Radium. Coloration of Substances by the Action of the Rays.—The radiation from radium causes phosphorescence in a great many substances : the salts of the alkalies and alkaline earths, uranyl-potassium sulphate, organic substances, cotton, paper, cinchonine sulphate, skin, glass, quartz, etc. The most sensitive substances are barium platinocyanide, willemite (silicate of zinc), sulphide of zinc, and diamond. With the penetrating β-rays willemite and the platinocyanide are the most sensitive, while

with the α-rays it is better to use phosphorescent sulphide of zinc.

Phosphorescent substances are altered by the prolonged action of the radium rays. They become less excitable and are less luminous under the influence of the rays. At the same time they change their color or become colored. Glass becomes violet, black or brown. Salts of the alkalies turn yellow, green or blue. Transparent quartz becomes smoky quartz. Colorless topaz turns yellow, orange, etc. Glass colored by radium is thermoluminescent. On heating it to 500° it emits light. At the same time it becomes colorless and returns to its original condition. It is then capable of being colored anew by the action of the rays of radium.

The salts of radium are spontaneously luminous. It might be said that they make themselves luminous by the action of the Becquerel rays they emit. Anhydrous chloride and bromide of radium are the salts that give the most intense luminescence. They may be obtained so luminous that the light can be seen in full daylight. The light emitted by the salts of radium recalls in tint that from a fire-fly. The luminosity of the radium salt decreases with time without ever completely disappearing, and those that were colorless at first become gray, yellow or violet.

Physiological Effects of the Radium Rays.—The rays from radium cause different physiological actions.

A salt of radium placed in an opaque box made of cardboard or metal acts on the eye and produces the sensation of light. To obtain this result, the box containing the radium is placed before the closed eye or against the temple. In this experiment the center of the eye becomes luminous by phosphorescence under the influence of the radium rays, and the light one sees has its source in the eye itself.

The rays of radium act on the epidermis. If we place on the skin for a few minutes a bulb containing radium no particular sensation is felt. But fifteen or twenty days afterward it produces a reddening of the skin, then a slough in the place where the bulb was applied. If the action of the rays be long enough there is finally formed a sore that takes several

months to heal. The action of the rays from radium is analogous to that produced by the Roentgen rays. The attempt has been made to utilize this action in the treatment of lupus and cancer.

The radium rays also act upon the nervous centers and cause paralysis and death. (Danysz.) They seem also to act with especial intensity upon growing tissues. (Bohn.)

The Employment of Radium in the Study of Atmospheric Electricity.—The radium rays have also been utilized in the study of atmospheric electricity (Paulsen, Witkowski, Moureaux). A small quantity of a salt of radium placed at the extremity of a metallic rod serves as a point of contact for the potential. By this very simple arrangement we can avoid the use of flames or of water-dropping apparatus to measure the potential at any point in the atmosphere.

III. The Heat Given Off by the Salts of Radium.

The salts of radium continually give off heat. Its amount is sufficient for it to be detected by means of a crude experiment with two ordinary mercury thermometers. Two identical heat-insulating vacuum-bulbs are used. In one of these is placed a glass bottle containing 0.7 gram of pure radium bromide ; in the second is placed a glass bottle containing some inactive substance, such as barium chloride. The temperature of the contents of each is shown by a thermometer placed with its bulb near the bottle. The mouths of the flasks are closed with cotton. Under these conditions the thermometer in the same flask as the radium always has a temperature $3°$ higher than that indicated by the other thermometer.

The quantity of heat given off can be estimated by means of a Bunsen ice calorimeter. By placing in the calorimeter a glass bottle containing a salt of radium, it is found that there is a continued supply of heat that stops as soon as the radium is removed. A determination made with a salt of radium that had been prepared a long time before shows that each gram of radium gives off 80 small calories an hour. Hence radium gives off enough heat to melt its own weight of ice every hour. Nevertheless the radium salt seems to re-

main in the same condition, and besides, not a single ordinary chemical reaction can be called in to explain such a continuous liberation of heat.

It has been shown, also, that a recently prepared salt of radium sets free a relatively small amount of heat. The heat set free in a given time then increases continually, and tends towards a definite value which is not quite reached at the end of a month.

When a salt of radium is dissolved in water and the solution enclosed in a sealed tube, the amount of heat given off at first is slight. It then increases and tends to become constant at the end of a month. When the limit is reached, the amount of heat given off from the radium in solution is the same as if it were in the solid state.

The amount of heat set free by radium at different temperatures can also be estimated by causing it to boil a liquefied gas and measuring the volume of gas that is liberated. The experiment can be performed with methyl chloride, which boils at $-21°$.

The experiment was also performed by Dewar and myself with liquid oxygen ($-180°$) and liquid hydrogen ($-252°$). The latter is especially suitable for the experiment. A tube, A, closed at the lower end and surrounded by a Dewar vacuum-bulb, contains a little liquid hydrogen, H. A delivery-tube, *tt*, allows the gas to be collected in a graduated

Fig. 1.
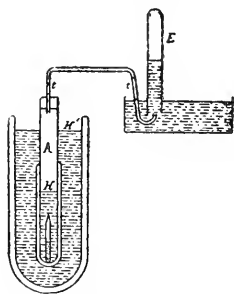
tube filled with water. The tube, A, and its insulator are plunged into a bath of liquid hydrogen, H'. Under these conditions no gas is produced in the tube A. When a bottle containing 0.7 gram of radium bromide is placed in the hydrogen in A, there is a continuous liberation of hydrogen gas, and 73 cc. of the gas are collected per minute. (The radium bromide had been made only ten days before.)

IV. Induced Radioactivity and Radioactive Emanations.

Induced Radioactivity.—Radium, thorium, and actinium

have the property of acting externally, apart from the Becquerel rays that they emit. They communicate little by little their radioactive properties to substances in their neighborhood, and the latter emit in turn Becquerel rays. The activity can be transmitted to gases, liquids, and solids. The phenomenon is known as induced radioactivity.

Induced radioactivity propagates itself in gases step by step by a sort of conduction, and is not at all due to direct radiation from the body which causes it.

When the activated substance is removed from the radioactive body, the induced radioactivity on it persists for a certain time. It diminishes, nevertheless, little by little and finally disappears.

Emanation.—To explain these phenomena, Rutherford supposes that radium and thorium are constantly giving off an unstable, radioactive, gaseous material, which he calls an emanation. The emanation spreads into the gas surrounding the radioactive substance. It destroys itself little by little by giving off Becquerel rays and by producing other unstable radioactive substances that are not volatile. These new substances attach themselves to the surface of solid bodies and render them radioactive.

Without stating so many hypotheses, we may adopt the name emanation to designate the radioactive energy in the form which it has when it spreads into the gas surrounding the radioactive substance. It may be supposed also, that this energy disappears in creating the energy of induced radioactivity in solids.

The Radioactivity Induced by Radium and the Emanation from Radium.—When a solid salt of radium is placed in a closed space filled with air, the interior walls of the closed space and all solids in it become radioactive. We may, for example, place inside the space a plate of any solid, leave it there a certain time, and then remove it to study its activity. It is found that the activity of the plate increases at first according to the length of its stay in the space, but that it reaches a limiting value after a sufficiently long time. When the ex-

cited plate is removed from the space it loses its activity according to an exponential law, the radiation falling to one-half its value in about half an hour. In a general way all solid substances under the same conditions acquire and lose their activity in the same manner.

The phenomena are much more intense (about twenty times), if instead of the solid salt of radium, we place a solution of it inside the closed space in an open vessel.

The nature and the pressure of the gas contained in the closed space have no influence upon the observed phenomena.

The induced activity in a closed space is proportional to the quantity of radium present.

When the space containing the radium communicates with a second by a tube, solids contained in the second become equally active after a sufficient time. The transmission of the activating property can even take place from one to the other through a capillary tube.

When the gas which has been made active by remaining in one space containing radium is passed into another, it retains for a considerable time the property of rendering radioactive solids that are brought in contact with it. The gas thus removed from the action of the radium gradually loses, nevertheless, its power of causing radioactivity. It disappears as a function of the time, according to an exponential law. It loses one-half of its value every four days.

To interpret this phenomenon it must be assumed that radium continuously gives off a constant radioactive emanation. This emanation spreads into the air in a closed space, and acting on solids, makes them radioactive. When the air is transferred to another space, the emanation is carried along with it. Finally, it is destroyed spontaneously with such velocity that the quantity of emanation in the gas diminishes by one-half every four days.

In a space containing radium there is established a state of equilibrium when the quantity of emanation in the space is such that the loss of emanation resulting from its spontaneous destruction is exactly compensated by the continued supply coming from the radium.

The following experiment can be performed : The glass receiver, A (Fig. II.), filled with air, communicates through the constricted part, O, with the bulb, B, which contains radium, S. At the end of a certain time the emanation has spread into A, and its interior walls have become active. The receiver, A, is then separated from the radium by closing O with a flame. The external radiation of A may then be studied by placing it in the interior cylinder of a cylindrical condenser (Fig. III.). The interior cylinder is of aluminium, BBBB. It is brought to a potential of 500 volts. The external cylinder, CCCC, of the condenser is of copper. It is in connection with an electrometer and piezoelectric quartz. By means of the quartz the current passing through

Fig. II.

the condenser is measured. This current is caused by the Becquerel rays that escape from the tube A, pass through the cylinder of aluminium B, and make the air between the two cylinders a conductor of electricity. The apparatus is surrounded by a protective metallic envelope, EEEE, connected with the earth.
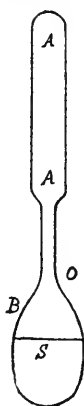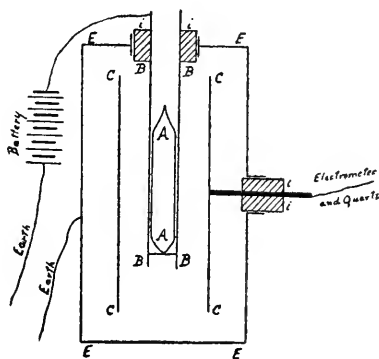
Fig. III.

It is found that the radiation from the tube A diminishes with time according to an exact exponential law, expressed by the equation

$$I = I_0 e^{-at}.$$

I_0 is the value of the radiation at the beginning of the time, I the value at the instant t, and a a constant coefficient. $a = 2.01 \times 10^{-6}$, taking one second as the unit of time. The radiation falls to one-half its value after about four days.

In a second experiment the tube A may be made active as before, and the interior can then be evacuated by pumping out the air containing the emanation. Under these conditions the radiation of the receiver, A, diminishes much more rapidly, and becomes twice as feeble in about half an hour. This law of loss of activity is the same as that according to which excited bodies lose their activity when they are exposed to the free air. The result is the same if inactive air be admitted to the receiver, A, after having been evacuated.

One is thus led to the conclusion that in the first experiment the activity of the receiver, A, is caused by the air charged with the emanation contained in the receiver, and that the law of the diminution of the radiation in this experiment represents as well the law of the spontaneous disappearance of the emanation.

When a vacuum is produced in the receiver, A, which contains air charged with the emanation, and when the radiation of the receiver is measured immediately after the extraction of the air, it is found that the radiation has not changed at the moment when the active air is withdrawn. The Becquerel radiation of air charged with the emanation does not, then, produce any action in this experiment. This radiation probably exists, but it is composed of very slightly penetrating rays, incapable of passing through the glass wall. In this connection the following experiment can be performed. One of the ends of the metallic tube, AAAA (Fig. IV.), communicates at O by means of a rubber tube with a receiver, B, in which is a solution of a radium salt. The other end of the tube, A, is closed with an insulating stopper, i. Through the stopper passes a metallic rod, C, connected with an electrometer. The tube, A, and the rod, C, form a cylindrical condenser. The tube, A, is brought to a potential of 500 volts. The metallic tube, DDDD, connected with the earth, serves as a guard-tube. When the tube, A, is sufficiently

active it is removed from the radium, and the intensity of the
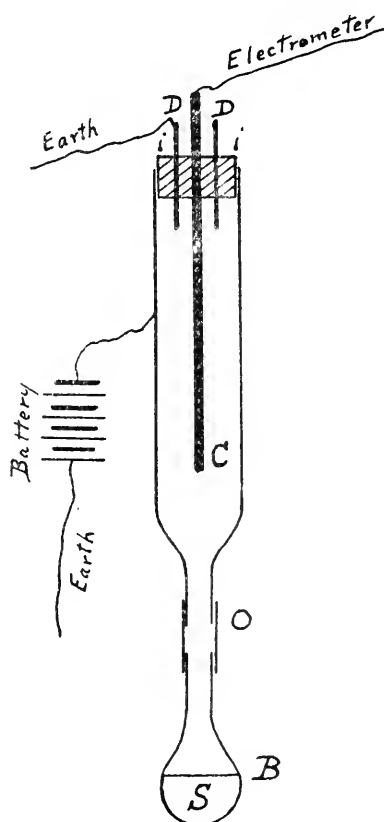
Fig. IV.

current passing through the condenser is measured. Then
the active air which fills the condenser is rapidly driven out,
inactive air is admitted, and a new measurement of the inten-
sity of the current is made immediately. It is found that the
current has become six times more feeble. Thus, during the
second measurement the radiation of the excited walls acts
solely to ionize the air in the condenser, while during the
first measurement the emanation acts as well. We may, then,
suppose that it also emits an emanation. This radiation is

necessarily very slightly penetrating, for its action cannot be detected on the exterior.

When a solid plate which has been excited by the emanation becomes inactive in free air, the law of loss of activity depends on the time during which the plate has been left in contact with the emanation. If the action of the emanation is prolonged (more than twenty-four hours, for example), the law of loss of activity is given by the difference between two exponentials. The intensity of ·the radiation, I, may in this case be represented as a function of the time, t, by the equation

$$I = I_0[Ke^{-bt}-(K-1)e^{ct}].$$

I_0 is the intensity of the radiation at the beginning of the time, that is at the moment when the plate is removed from the influence of the emanation. K, b, and c are three constant coefficients : K = 4.2 ; b = 0.000413 ; c = 0.000538, taking one second as the unit of time.

These results are represented by the curve 1 (Fig. V.). The logarithm of I is represented on axis of the ordinates, and the time on the axis of abscissas. One hour and a half after the beginning of the loss of activity the second exponential has become negligible with respect to the first in the expression for the value of I, and the representative curve has become straight. From this moment the activity diminishes by one-half during each period of twenty-eight minutes.

If the duration of the action of the emanation is not so long, the law of the variation of the radiation during its loss is much more complex. In Fig. V. are represented the results of experiments for different times of action, as indicated on the corresponding curves. We see, for example, that for a time of excitation of five minutes, the intensity of the radiation during the loss of activity first falls rapidly to a minimum ; then it increases, and again begins to fall. Finally, the law of loss of activity tends towards a simple exponential law which is the same as the limiting law after prolonged excitation. These complex phenomena can be explained by assuming that on the excited plate the radioactive energy is in three distinct states, but the demonstrations relative to this subject are too long to have a place in this article.

The emanation from radium causes the energetic phosphor-
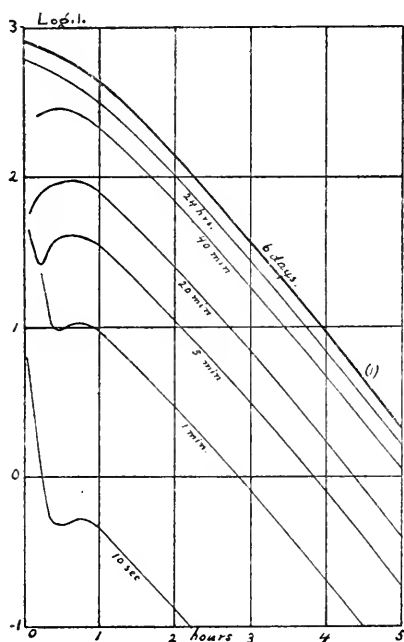
Fig. V.

escence of a large number of substances. Glass reservoirs containing air charged with the emanation are luminous, Thuringian glass being the most sensitive. Phosphorescen sulphide of zinc is particularly sensitive to the action of the emanation from radium, and then gives an intense light.

If in a closed space substances become more active the greater the amount of free gas around them. When plates placed parallel to one another, and a short distance apart, are put into a closed space with radium, the faces of each plate become excited in proportion to its distance from the others. When glass tubes of different diameters are filled with the emanation and communicate with one another, the walls of those of greatest interior diameter become most active. These tubes are also most luminous. To interpret these facts it must be assumed that the air charged with the emanation acts

on the walls by a radiation that arises in every part of the gaseous mass, and that the radioactivity induced upon a wall is proportional to the flow of exciting radiation received by that wall.

The Slow Evolution of Induced Activity.—A solid body acquires a very feeble, persistent, induced activity when it remains a month or less in contact with the radiation from radium. A substance withdrawn from the influence of the emanation after having been subjected to it for a long time loses its activity rapidly at first, according to the laws given. But the activity of the radiation does not disappear completely. There remains a radiation several thousand times more feeble than it was at first. This radiation is given off with extreme slowness and continues for several years. (The radiation passes through a minimum, then slowly increases for several months, but always remains very slight.)

Occlusion of the Emanation of Radium by Solids.—All solids when excited by contact with the emanation from radium acquire the property of themselves emitting the emanation in very small quantity. They preserve this power for only twenty minutes from the time they are removed from the space containing the emanation. Nevertheless certain substances as caoutchouc, paraffin, and celluloid have the property of being saturated with the emanation, and of emitting it afterwards in abundance for several hours, or even days.

Induced Activity of Liquids.—When a liquid is placed in a closed space with radium it becomes radioactive. Water, salt solutions, petroleum, etc., can thus be excited. The liquids dissolve a certain amount of the emanation. When an excited liquid is separated from the radium and sealed up in a tube it slowly loses its activity according to the law of the destruction of the emanation (decrease to one-half in four days). When the liquid is placed in a flask open to the air it loses its activity very rapidly, and the emanation spreads into the surrounding air.

Variations of the Activity of Solutions of Radium Salts and of the Solid Salts of Radium.—When a solution of a salt of radium

is exposed to the air of a room in an open vessel it becomes almost inactive. The solution emits an emanation that spreads into the room and causes induced radioactivity of the walls. The radiation of the radium is thus externalized. If the solution be enclosed in a sealed tube its activity increases little by little, and tends toward a limiting value that is reached only after several months. No doubt the emanation produced by the radium accumulates in the tube until the velocity of its spontaneous destruction is equalized by the supply from the radium.

We have seen that a salt of radium that has been freshly prepared possesses an activity which increases with the time, and becomes about five times as great as the initial activity. It seems that the emanation emitted by the radium can escape only with difficulty from the solid salt, and that it accumulates there and is transformed at once into induced radiation. An equilibrium is established when the spontaneous loss becomes sufficient to compensate the production.

When solid salt of radium is heated to redness, all the emanation which it had accumulated escapes. When the salt returns to the temperature of the room it emits Becquerel rays to a much less extent. However, the radiation recovers little by little its original value, which is reached after one or two months. The salt which had been heated to redness no longer possesses the power of emitting the emanation, but this property may be restored to it by dissolving it and drying it at a slightly elevated temperature.

Diffusion of the Emanation from Radium.—Danne and I have studied the law of the diffusion of the emanation of radium. A large glass reservoir filled with excited air communicates with the atmosphere by means of a capillary tube. The Becquerel radiation emitted by the walls of the reservoir is measured as a function of the time, and from this is deduced the law of the escape of the emanation through the capillary tube. It is found that the rapidity of the escape of the emanation is proportional to the quantity of it in the reservoir. It varies proportionally to the cross section of the capillary tube, and inversely as its length. These laws are the

same as for a gas mixed with air under the same conditions. The coefficient of the diffusion of the emanation into air is equal to 0.100 at 10°. The coefficient is, therefore, of the same order of magnitude as that of the diffusion of carbon dioxide into the air, which is equal to 0.15 at the same temperature.

Radioactivity Induced by Thorium and the Emanation of Thorium.—Thorium emits an emanation and gives rise to the phenomena of induced radioactivity. These properties have been made the subject of numerous researches by Rutherford. The action of thorium is, otherwise, considerably less intense than that of radium.

The emanation of thorium disappears spontaneously according to a simple exponential law, but its disappearance is much more rapid than that of the emanation of radium. The quantity of the emanation from thorium diminishes by one-half in about one minute and ten seconds, while in the case of radium the quantity falls to one-half in four days. This considerable difference causes a profound difference in the aspect of the phenomena.

In a closed space of not too great dimensions the emanation from radium spreads almost uniformly into all parts. But under the same conditions the emanation of thorium is found to accumulate in the vicinity of the thorium, because it disappears spontaneously before it has time to diffuse any considerable distance into the air.

The radiant activity of a substance can be measured by placing it upon the lower plate of a condenser formed of two horizontal plates, and measuring the conductivity communicated to the air between the plates. If this measurement be made with oxide of thorium, it is found that the conductivity of the air is greatly decreased when a current of air is sent between the plates. The oxide of thorium emits, indeed, an emanation that accumulates upon the substance and by its radiation helps to ionize the air between the plates. A current of air carries away the emanation as rapidly as it is set free, and the only thing left to cause ionization is the Becquerel radiation coming directly from the thorium.

If the same experiment be repeated with a salt of radium it is found that the current of air produces only a feeble effect. With uranium and polonium, which do not emit the emanation, the current of air has no effect. On the contrary, in the case of actinium, the action of the current of air is to suppress four-fifths of the conductivity of the air. It may be concluded that for thorium, and especially for actinium, the radiation of the emanation is very important in comparison with the radiation of the radioactive substance itself.

When one wishes to excite a solid to saturation with the emanation from thorium, it is necessary to cause the emanation to act for a long time, and hence new supplies of it must be brought continually to the surface of the body that is to be excited. To do this a current of air is passed through a solution of a salt of thorium and, then this current, of air charged with the emanation, is passed over the body. The solid, when excited by the emanation from thorium, loses its activity spontaneously according to an exponential law. The radiation falls to one-half every eleven hours. Hence, contrary to what takes place with the emanations, the activity induced by thorium upon solid substances disappears more slowly than that induced by radium.

Radioactivity Induced by Actinium and the Emanation from Actinium.—Actinium emits an emanation which gives a very intense radiation. This emanation disappears spontaneously with extreme rapidity, and diminishes by one-half in about one second. In air at the atmospheric pressure the emanation emitted by actinium cannot propagate itself to a greater distance than 7 or 8 mm. from the active substance, and excites bodies only when they are placed very near the source. On the contrary, in a vacuum the diffusion is rapid, and a body placed 10 cm. away from the actinium can be excited. The radioactivity induced by the actinium upon solids disappears according to an exponential law. It diminishes to one-half in about thirty-six minutes.

The Concentration of Induced Radioactivity upon Bodies Charged Negatively.—Rutherford showed that a body exposed to the emanation from thorium became much more active

when it was charged negatively than when it was at the same potential as the surrounding objects. On the contrary, it became less excited when it had a positive potential. The same phenomenon is noticed in the case of the excitation by radium and actinium. The nature of this curious phenomenon seems to me not to be well established.

Condensation of the Emanations from Radium and Thorium. —Rutherford and Soddy discovered that the emanations from radium and thorium can be condensed at the temperature of liquid air. A current of air charged with the emanation loses its radioactive properties when passing through a coil of tube plunged in liquid air. The emanations remain condensed in the tube, and can be restored to the gaseous state when it is warmed. The emanation from radium condenses at $-150°$, while that from thorium condenses between $-100°$ and $-150°$. The experiment can be performed as follows : Two glass reservoirs, one large and the other small, communicate with one another. They are filled with gas excited by radium. The small reservoir is plunged in liquid air. The large reservoir then rapidly becomes inactive, while all the activity is concentrated in the small reservoir. If the two are then disconnected, and the small one be taken from the liquid air, it is seen that the large reservoir is not at all luminous, while the small one gives off more light than at the beginning of the experiment. The experiment is a very brilliant one if the walls of the reservoirs are coated inside with phosphorescent sulphide of zinc.

When a platinum wire excited by thorium or radium is heated to redness, it loses most of its activity. Fanny Cook Gates showed that this radioactivity is transferred to cold solids placed in the vicinity of the wire. It distils in some way, at a sufficiently high temperature, passing through the intermediate form of a gaseous emanation. The induced radioactivity of solids would thus be analogous to a condensed emanation.

Activity Induced by Remaining in Solution in a Radioactive Liquid. Uranium X. Thorium X.—Certain substances are temporarily excited when they stay in the same solution with

radioactive substances. Giesel and Mme. Curie prepared active bismuth by dissolving one of its salts in the solution of a salt of radium. Debierne also excited a salt of barium in a solution of a salt of actinium. The barium salt thus excited presents certain analogies to the salt of radium, and can be fractionated in the same way. By crystallization the active chloride is concentrated in the salt that is deposited.

By various methods of chemical precipitation the activity of uranium has been divided (Crookes, Soddy, Rutherford and Grier, Debierne, Becquerel). For instance, barium chloride is added to a solution of uranyl nitrate, and the barium is then precipitated by adding a little sulphuric acid. The precipitated barium sulphate, when separated and dried, is radioactive. It has carried with it a part of the activity of the uranium, for the uranium salt, when the solution is evaporated to dryness, is less active than before it was submitted to this operation. But after several months the sulphate of barium loses its radioactivity, while the uranium salt has regained its original properties. It is evident that the barium was excited by contact with the uranium, or that it occluded in some special form a part of the activity of the uranium (uranium X of Crookes).

Rutherford and Soddy showed that if nitrate of thorium is precipitated by ammonia, the precipitated oxide of thorium is less active than ordinary thorium. The liquid from which it was precipitated is radioactive, and on evaporating it to dryness the small residue is 2,500 times more active than the thoria (they call the radioactive substance in this residue thorium X). After several weeks the residue has lost its activity, the thorium X has disappeared, and the thoria which was precipitated has, on the contrary, regained its normal activity. Further, while the thorium X existed it emitted the thorium emanation in abundance.

Rutherford and Soddy think that uranium X and thorium X are simply intermediate products of the breaking down of uranium and thorium. Thorium, for example, produces thorium X continuously, which breaks down into the emanation of thorium, that is in its turn transformed into induced activity.

Conductivity of Atmospheric Air. Emanation and Induced Radioactivity at the Surface of the Earth.—Elster and Geitel, and also Wilson, showed that atmospheric air conducts electricity to a slight extent, that it is always slightly ionized. This ionization seems to be due to various causes. According to the work of Elster and Geitel, atmospheric air always contains a small proportion of an emanation analogous to that emitted by radioactive substances. Metallic wires suspended in the air and kept at a high negative potential become active under the influence of this emanation. At the summits of high mountains the atmosphere contains more of the emanation than on plains or at the level of the sea. The air of caves and caverns is especially highly charged with the emanation. Air rich in the emanation can also be obtained by aspirating, by means of a tube sunk in the earth the air which is contained in it. The air extracted from certain mineral waters contains the emanation, while the air dissolved in the water of the sea and of the rivers is almost free from it.

The conductivity of the atmosphere is also probably due in part to very penetrating radiations that traverse space, and of which the origin is unknown. Finally, it is probable that all bodies are slightly radioactive, and that those at the surface of the ground render the air around them a conductor of electricity.

Time-Constants that Characterize the Disappearance of Emanations and of Induced Radioactivity.—We have seen that the radioactive emanations and the induced radioactivity of solids disappear spontaneously, and that the law of their disappearance is, in general, a simple exponential law. The intensity of the radiation, I, is given as a function of the time, t, by the formula,

$$I = I_0 e^{-at}.$$

I_0 is the intensity of the initial radiation, and a a constant. This exponential law is completely defined by the knowledge of a constant of time that may be, for example, the inverse of a in the preceding formula. One may also take as the con-

stant the time necessary for the intensity of the radiation to diminish to one-half.

It is very remarkable that these constants of time seem to be invariable under widely different circumstances. Thus it is that the emanation from radium diminishes to one-half during each period of four hours, whatever may be the conditions of the experiment, and whatever the temperature between —180° and +450°. The rate of its disappearance is the same whether the emanation be in the gaseous state (room temperature) or condensed (—180°). The properties of the emanation from radium thus give us an invariable standard of time which is independent of all agreements as to the unit.

The time-constants of the radioactivity serve to characterize in a precise manner the nature of the different radioactive energies.

The following are the times necessary for the activity to fall to one-half of its value :

Emanation of	Time.
Radium	4 days
Thorium	1 minute 10 seconds
Actinium	Several seconds
Induced radioactivity of	
Radium	1 hour (after beginning of the loss. 28 minutes (for t i m e s more than two hours after the beginning of the loss)
Thorium	11 hours
Actinium	36 minutes

Thus J. J. Thomson and Adam found recently that the emanation from water from certain sources falls to one-half for each period of four days, and that this emanation causes induced activity in solids which falls to one-half in about forty minutes. The supposition is that the emanation contained in the water is due to radium.

Ordinary thorium extracted from monazite sand is slightly radioactive. Thorium from pitchblende is strongly radioactive (thorium with actinium of Debierne). The radioactivity

in the two cases is not due to the same substance, for the time-constants of the emanation and of the radioactivity are different.

Certain radioactive substances like actinium have never been separated in a pure state, and it may be supposed that the very active substances that have been studied contain only traces of them. The chemical reactions of substances cannot be recognized with certainty when they are found solely in a diluted condition, mixed with other substances. Under those circumstances one element may carry another down with it in a precipitation, and the action of the reagent is not the same as when we have pure compounds. Hence the chemical reactions will not serve to characterize a radioactive substance. It may, however, be recognized under all circumstances by the time constants of the emanation it emits, and of the induced radioactivity excited by that emanation upon solids.

Nature of the Emanation.—According to Rutherford, the emanation of a radioactive substance is a radioactive, material gas which escapes from it. In fact, the emanation from radium acts in many ways like a gas.

When we put in communication two glass reservoirs, one containing the emanation and the other none, the emanation diffuses into the second and, when equilibrium is established, it is found that the emanation is divided between the two reservoirs according to their respective volumes. One of the two may be heated to 350°, while the other remains at the room temperature, and it is found that in this case, also, the emanation is divided between the two reservoirs as if it were a perfect gas obeying the laws of Marriotte and Gay-Lussac.

We have also seen that the emanation from radium diffuses into the air according to the law of the diffusion of gases, and with a coefficient of diffusion comparable with that of carbon dioxide. Finally, the emanations from radium and thorium condense at low temperatures like liquefiable gases.

At the same time it should be remembered that no one has yet observed any pressure due to the emanation, nor has any one shown by weighing that a material gas is present. All

our knowledge of the properties of the emanation results from measurements of radioactivity. More than that, no one has yet shown with certitude that there is a characteristic spectrum produced by the emanation.

The emanation should also not be considered as an ordinary material gas, for it disappears spontaneously from a sealed tube containing it, and the rapidity of its disappearance is absolutely independent of the conditions of the experiment, especially of the temperature.

It is very curious that the numerous attempts made under the most varied conditions to obtain chemical reactions with the emanation have been fruitless. To explain this fact Rutherford thinks that the emanations are gases of the argon family.

The following facts are difficult to explain. The emanation from radium condenses at —150°, and according to Rutherford, a current of air at —153° may be passed over it continuously without removing it. The amount of the emanation must be very small, and if it had the slightest tension at —153°, it would quickly evaporate in a current of air. Further, the temperature of condensation by cooling should be a function of the amount of the emanation in a given volume of air, which has not yet been proved.

Debierne and I have found that the emanation passes with extreme ease through the tiniest holes and fissures in solids, while under the same conditions the ordinary gases could circulate only with the greatest slowness.

Rutherford supposes that radium destroys itself spontaneously, and that the emanation is one of the products of the breaking-down. Debierne and I observed that a solid salt of radium quite rapidly excites the walls of the reservoir filled with air, which contains it, by the emanation which it emits. On the contrary, if a quite perfect vacuum be made in the reservoir the excitation takes place only with extreme slowness; but it rapidly reappears when a gas has been admitted. However, the emanation spreads much more rapidly in a gas at very low pressure than at the atmospheric pressure. It seems from this that the emanation experiences some par-

ticular difficulty in escaping from radium which is in a
vacuum.

*Disengagement of Gas by the Salts of Radium. Production
of Helium.*—Giesel noticed that solutions of radium bromide
continually give off gases. These gases are principally hy-
drogen and oxygen, in the same relative proportion as in
water, and might, therefore, come from the decomposition of
the water of the solution. But Ramsay and Soddy also
showed that there always is a small quantity of helium that
they detected by its spectrum in a Geissler tube. The helium
lines were also accompanied by three unknown lines.

A solid salt of radium also constantly gives off gases capa-
ble of producing a pressure in a closed tube. To this libera-
tion of gas can be attributed two accidents during my experi-
ments. A sealed bulb of thin glass, almost filled with well-
dried bromide of radium, exploded and became slightly warm
at the same time. An explosion was also caused by dry
radium chloride when heated quite rapidly in a vacuum to
300°. In this case the explosion seemed to be caused by
fragments of the solid salt filled with occluded gas.

At the moment we dissolve in water a solid salt of radium
that has been prepared a long time, there is an abundant
evolution of gas.

The spontaneous production of helium in a sealed tube
containing radium is plainly a new fact of fundamental im-
portance. Ramsay and Soddy accumulated some of the
emanation from radium, and enclosed it in a Geissler tube at
low pressure. They obtained new lines which they attribu-
ted to the emanation, and they also showed that the spectrum
of helium was absent at first, but that it came into being little
by little in the tube. According to that, helium must be one
of the products of the disintegration of radium.

In support of the preceding results may be mentioned some
points noticed by Mme. Curie and me at the beginning of our
work. We were struck by the simultaneous occurrence of
uranium, radium, and helium in the same mineral. We took
50 kilograms of commercial barium chloride, coming from
minerals that did not contain uranium, and submitted it to

fractional crystallization to see whether it contained traces of radium chloride. After a prolonged fractionation, the portion at the head, now reduced to a few grams, was not at all radioactive. Hence, barium contains radium only when it comes from uranium minerals. These are the same that contain helium. One might think that there is a relation of cause and effect from the simultaneous occurrence of these three substances.

This rapid summary of the researches on radioactivity serves to show the importance of the scientific movement that has been started by the study of this phenomenon. The results obtained are of a nature to modify the ideas one might have about the invariability of the atom, the conservation of matter and of energy, the nature of the mass of bodies, and the energy spread through space. The most fundamental questions of science are thus brought into the discussion. Apart from the theoretical interest of which they are the object, the phenomena of radioactivity give new means of action to the physicist, the chemist, the physiologist, and the physician.

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NOTE.

To the Editor, American Chemical Journal :

In the February number of the AMERICAN CHEMICAL JOURNAL appeared an article by Keiser and Forder, suggesting still another method for solving the long vexed problem of the determination of free lime in cements. Every cement chemist in the world would welcome with pleasure even an approximately accurate method which could always be depended upon for distinguishing between the lime which is combined with the silica, and that which remains free in cements. Up to the present time, there have been 53 researches, comprising 25 different methods of attack, published on this subject. (See Ztschr. angew. Chem., **20**, 466.). As a matter of fact, the problem remains to-day unsolved.

Keiser and Forder, after speaking of the objections to the use of water or watery solutions, as a method of attack, proceed to describe a method in which a small fraction of a gram of cement is wetted with water, then subsequently dried and weighed. Every cement chemist knows that on wetting cement the tri-calcic silicate is quickly broken down with an accompanying formation of calcic hydroxide. We are now told that if free lime is already present the reaction will not proceed in that direction, or at least not quickly enough to involve the basic silicates present. It seems difficult to believe, in the light of past investigation, that this is possible. It would almost seem that the authors were not aware that methods involving the use of absolute alcohol have been abandoned, as it has been shown that even alcohol breaks down tri-calcic silicate with the formation of free lime.

Jordis and Kantner have pointed out in a most comprehensive article (loc. cit.) the harm that has been done by the

attempt to draw important deductions from data yielded by similar analytical methods. Is history to repeat itself?

A. S. CUSHMAN.

ROAD MATERIAL LABORATORY, BUREAU OF CHEMISTRY,
WASHINGTON, D. C., Feb. 12, 1904.

REVIEWS.

PRAKTISCHE UEBUNGEN ZUR EINFÜHRUNG IN DIE CHEMIE. Von DR. ALEXANDER SMITH, Professor für Chemie an der Universität Chicago. Nach einer vom Verfasser besorgten Umarbeitung der zweiten amerikanischen Auflage ins Deutsche übertragen von PROFESSOR DR. F. HABER und DR. M. STÖCKER. Karlsruhe: G. Braun, 1904,

In the preface, Professor Haber gives at some length his reasons for making this translation. He refers to the fact that the teachers of chemistry in American universities and colleges have frequently studied in Germany, and says that while American teachers with one accord pursue German methods of instruction in advanced chemical work, probably not one of these teachers has copied the German method of instructing beginners in the laboratory, commencing with systematic qualitative analysis, and entirely omitting work on general chemistry. Professor Haber finds the American method of beginning laboratory work by study of general chemistry the better of the two, and wishes his countrymen to try it.

German and American laboratory usage differ in that the tendency here is perhaps to over-coddle the beginner, while in Germany, in the past at least, it has been to neglect him.

Dr. Haber does not seem to know that this is not the first book of the American school which has been translated into German. Seubert made a translation of Remsen's Introduction to the Study of Chemistry, which was published in Tubingen in 1887, and in Stuttgart in 1895. This book, *if used properly*, covers practically the same ground in laboratory work in general chemistry as Dr. Smith's book.

It is to be hoped that these translations of American methods may in time help the beginner in the German laboratory, as Dr. Haber wishes and hopes, but this hope will not be realized until the laboratory teacher and his assistants really give their best effort and their entire effort during the laboratory hours to instruction.

That Dr. Haber too realizes this is evident, for he says in the preface that this method requires the constant supervision of the teacher and assistants, of whom one should be alloted to ten or at most twenty students.

Professor Smith's book is not a text-book, but a laboratory manual and an excellent one. It differs in three essentials from most books covering the same ground. First, it begins by explaining quantitative use of balance and of measuring apparatus with application to simple physical laws, *i. e.*, specific gravity of liquids and solids, laws of Gay-Lussac and Boyle. Further quantitative experiments on combining weights, multiple proportions, molecular weights, etc., are scattered through the book. Second, under the heading "Ion reactions and reactions between acids, bases and salts," a few simple experiments illustrating the dissociation theory are introduced. Third, the book contains no equations and is full of questions, and demands that the student shall write the equations in his note-book and shall study text-books to find answers to questions.

These last excellent features, which compel the thought and attention of the student, were first systematically used twenty-five years ago by Professor Volhard, now of Halle, at that time of Munich, in his admirable notes on qualitative analysis, which are still in use in the Munich laboratory. Dr. Haber informs us that Dr. Smith received his chemical education in Munich; it is possible that study with Volhard led him to use this method in his manual, which now, if Dr. Haber's hopes are fulfilled, may supply an undoubted want in German laboratory instruction.

HYPOCHLORITE UND ELEKTRISCHE BLEICHE. TECHNISCH-KONSTRUK-
TIVER THEIL. Von VIKTOR ENGELHARDT, Oberingenieur und Chef-
chemiker der Siemens und Halske Aktien-Gesellschaft, Wien.
Mit 266 Figuren und 64 Tabellen im Text. Halle a. S. Wilhem
Knapp, 1903. Preis M. 12.

This book is the eighth volume of the "Monographien über angewandte Elektrochemie." The name of the author is a guarantee for thorough work. He treats the subject of electric bleaching in two volumes, of which the present is devoted to the technical and constructive side and to the patent literature; the second volume, which will be published later, is to include the practical application of various methods with reference to relative profit, the analysis of raw materials and products, and the theoretical side of the subject.

It follows that while the present volume contains little of interest to most chemists, it is of great interest to those engaged in the manufacture of "bleach." Ninety-three patented methods are described, the more important ones in great detail, with abundant illustrations. Of special interest are the tabulated summaries, giving descriptive data, com-

parative efficiency, and relative expenses of the different systems.   E. R.

JAHRBUCH DER CHEMIE : Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. BECKURTS, Braunschweig ; C. A. BISCHOFF, Riga ; M. DELBRÜCK, Berlin ; O. DOELTZ, Clausthal ; J. M. EDER, Wien ; P. FRIEDLAENDER, Wien ; C. HAEUSSERMANN, Stuttgart ; A. HERZFELD, Berlin ; F. W. KÜSTER, Clausthal ; W. KÜSTER, Tübingen ; J. LEWKOWITSCH, London ; A. MORGEN, Hohenheim ; F. QUINCKE, Leverkusen ; A. WERNER, Zürich. Herausgegeben von RICHARD MEYER, Braunschweig. XII, Jahrgang, 1902. Braunschweig : Druck und Verlag von Friedrich Vieweg und Sohn, 1903.

This excellent and most acceptable report continues to fulfill the expectations of chemists, and it may now be regarded as indispensable.   A few changes and additions have been made to the staff of co-workers.   Professor A. Werner and Dr. Pfeiffer, of Zurich, have prepared the chapter on Inorganic Chemistry in place of Professor Muthmann.   A special examination of this chapter shows, as was to be expected, that the work is well done.   A new section in the inorganic chemical industries has been added.   This has been prepared by Dr. F. Quincke, of Leverkusen.   It is interesting to note that the contact process for the manufacture of sulphuric acid has led to attempts to devise a contact process for the manufacture of nitric acid by conducting a mixture of ammonia and atmospheric air over heated metals or metallic oxides.   It is stated that the manufacture of nitric acid from the air by means of electric sparks cannot be carried out economically in Germany.   But these are details.   Almost every page is of interest to the working chemist.   I. R.

JAHRBUCH DER CHEMIE : Heausgegeben von RICHARD MEYER, Braunschweig.   General Register über die Jahrgänge 1891 bis 1900 (Bände 1 bis 10).   Bearbeitet von W. WEICHELT, Korpsstabsapotheker, A. D., Coblenz.   Braunschweig : Druck und Verlag von Friedrich Vieweg und Sohn, 1903.

This index to the first ten volumes of the Jahrbuch seems to have been carefully prepared.   Wherever the ten volumes are found there this index should be also.   It covers 319 pages and is clearly printed.

AMERICAN

CHEMICAL JOURNAL

Contribution from the Kent Chemical Laboratory of the University of Chicago.

A STUDY OF HYDROLYSIS BY CONDUCTIVITY METHODS.

By Julius Stieglitz and Ira H. Derby.

In aqueous solutions of the hydrochlorides of weak bases the salts are partially hydrolyzed as represented by the equation :

$$RNH_3Cl + H_2O \rightleftharpoons RNH_3OH + HCl. \qquad (1)$$

The analytical determination of the proportions of free acid, base, and salt in such solutions is a matter of importance, because from the data obtained the affinity constants of the weak bases can be calculated.[1] The most accurate method of analysis is that of Walker,[2] who determined the amount of free acid by catalysis of methyl acetate. But the most rapid method is undoubtedly the one based on conductivity measurements of the solutions, as developed by Walker, and especially by Bredig. In an investigation of the velocities of rearrangement of o-aminophenyl alkyl carbonates in solutions of their hydrochlorides,[3] one of us recently had occasion to require an almost instantaneous method of analyzing such solu-

[1] Arrhenius : Ztschr. phys. Chem., **5**, 17 (1890) ; Bredig : *Ibid.*, **13**, 213, 321 (1894).
[2] *Ibid.*, **4**, 319 (1893).
[3] Stieglitz and Upson : This JOURNAL, **31**, 458 (1904).

tions, the proportion of free acid increasing rapidly and continuously by the process of rearrangement, as expressed summarily in

$$(Acyl\,O)RNH_3Cl \rightleftharpoons HO.R(NH\,Acyl) + HCl. \quad (2)$$
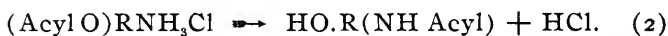
The conductivity method was the only one sufficiently rapid for the purpose.

The directly observed molecular conductivity M_v of such a solution is made up of the conductivity μ_v of the non-hydrolyzed salt and the conductivity μ_{HCl} of the free acid, since the conductivity of the free weak base can be neglected as minimal in the presence of its salt. If x represents the percentage of hydrolyzed salt, then, according to Walker,

$$M_v = (1-x)\mu_v + x\mu_{HCl}, \quad (3)$$

and
$$x = \frac{M_v - \mu_v}{\mu_{HCl} - \mu_v}. \quad (4)$$

In the application of this equation various investigators have given different interpretations to the value of μ_{HCl}, the molecular conductivity of hydrochloric acid. Walker considered it to be the molecular conductivity of the acid for the original concentration of the salt solution, *i. e.*, for a completely hydrolyzed salt. Bredig, to whom we owe the most important work in the establishment of the method, used the value 383[1] as "the nearly constant molecular conductivity of the free hydrochloric acid at 25°." This is also the interpretation used in Vaubel's Physikalische Methoden der Quantitativen Bestimmung Organischer Verbindungen.[2] Winkelblech, working under Bredig, later again used Walker's interpretation.[3] Ley,[4] in an extended and important study of hydrolysis, took for μ_{HCl} the molecular conductivity of hydrochloric acid at infinite dilution, 393. Of these various interpretations, the one of Walker seemed to us the most trustworthy on the basis of the following views :

If in an n-th normal solution of a hydrochloride such as

[1] In reciprocal mercury units.
[2] P. 292 (1902).
[3] Ztschr. phys. Chem., **36**, 356 (1901).
[4] *Ibid.*, **30**, 193 (1899) ; also Ber. d. chem. Ges., **34**, 2626 (1901).

aniline hydrochloride, x per cent of the salt is hydrolyzed, the hydrochloric acid formed, no matter how little of it is produced, does not ionize to the same degree as it would if it were dissolved alone in all the water present. It has the chlorine ion in common with the salt. We can assume the acid as sharing the water with the salt[1] in the proportion of $x : (1—x)$, producing a mixture of x cc. n-th normal hydrochloric acid and $(1—x)$ cc. n-th normal non-hydrolyzed aniline hydrochloride. Both the acid and the salt being nearly equally ionized in equivalent solutions, they would contain the common ion in almost equal concentrations and form approximately isohydric solutions. Each would then have the molecular conductivity of the n-th normal solution.

If such is the case equation (4) would read

$$x = \frac{M_v - \mu_v}{\mu_{HCl(v)} - \mu_v}, \tag{5}[2]$$

the symbols having the same significance as in (4) excepting that $\mu_{HCl(v)}$ is always the molecular conductivity of hydrochloric acid for the original concentration of the salt solution used. If the degree of hydrolysis becomes very large, for instance 50 per cent and more, equation (5) would still hold, as we have simply mixtures containing larger proportions of the isohydric acid, of the same normality as before. If, as in the case under investigation by one of us, by a rearrangement of a salt according to (2) the free acid should accumulate more and more and finally be the sole electrolyte present—the salt disappearing in proportion as the acid is formed—equation (5) would hold continuously. If an excess of acid were added to the original solution, a similar determination of the total free acid could still be made (see below).

In the development of (5) two assumptions have been made. The first is that in equivalent dilute solutions the de-

[1] Arrhenius: Ztschr. phys. Chem., **2**, 288 (1888) and **31**, 206 (1899).

[2] Another form of the same equation is:

$$x = \frac{k_{obs} - k_v}{k_{HCl(v)} - k_v}, \tag{5}$$

in which the symbols stand for the respective specific conductivities. Since specific conductivities are found before the molecular, it is often more convenient to use this form of the equation.

grees of ionization of the salt and free acid may be considered to be practically the same—an assumption which is not absolutely true but which is frequently made in similar cases. For N/32 solutions of hydrochloric acid and potassium chloride the degrees of ionization are 97 and 90 per cent respectively. The second assumption is that solutions of equal concentrations of a given common ion may be considered isohydric. This has been proved to be true for weak acids which obey Ostwald's dilution law[1] and is also true as a matter of experience for strongly ionized substances such as ammonium and potassium chlorides.[2]

In view of the difference shown in the interpretation of Walker's formula, as explained above, it was thought best to test by means of mixtures of a salt and of a strong acid, of known content, its range of reliability, particularly for very strongly hydrolyzed solutions containing much acid.[3] Two series of experiments were made. The first was intended to test the application of (5) to the analysis of mixtures of hydrochloric acid and potassium chloride of varying concentrations but especially for N/32 solutions of each. In the second place equation (5) was used to ascertain the condition of equilibrium in solutions of aniline hydrochloride containing an excess of hydrochloric acid.

Potassium Chloride and Hydrochloric Acid.

The measurements were made with the Kohlrausch apparatus. The wire of the Wheatstone bridge was 1 meter long and was carefully calibrated as were all the resistances, burettes, and pipettes used. The temperature was kept constant at 25° (±0.01°) by means of a large thermostat built according to Ostwald's principles. The measurements were made largely in Kohlrausch vessels, partly in those of the Arrhenius type. The acid used was repeatedly standardized against Iceland spar[4] and against sodium carbonate. The water used had a specific conductivity of 2.0×10^{-6}. Table

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[1] Arrhenius : Lehrbuch der Elektrochemie, p. 179 (1901).

[2] Arrhenius : Ztschr. phys. Chem., **31**, 206 (1899).

[3] Such solutions were to be studied by this method.

[4] Chem. News, **81**, 73 (1897) ; **87**, 5 (1903). Platinum vessels were used.

I., following, gives the results of a first series of measurements with N/32 solutions. The first column gives the observed specific conductivity, the second the specific conductivity calculated according to (5) from the known composition of the mixture on the assumption that the two N/32 solutions are isohydric. The third column gives the percentage of acid used in parts of the total volume of electrolyte ; column 4 gives the percentage of acid found as calculated with the aid of equation (5) or (5′). The last column gives the percentage of acid found as calculated when μ_{HCl} is made 383. If μ_{HCl} is taken as μ_{∞} or 393, the values found would be still lower than the ones given in this column :

Table I.

$10^6 \times k_{obs.}$	$10^6 \times k_{calc.}$	Per cent acid used.	Per cent acid found. (Equation 5′.)	Per cent acid found. ($\mu = 383$.)
3978		0.00	0.00	0.00
4625	4670	8.92	8.34	8.10
5274	5322	17.33	16.71	16.22
5711	5766	23.00	22.34	21.68
6156	6227	29.00	28.08	27.26
6535	6590	33.68	32.96	32.00
6852	6902	37.69	37.05	35.95
7116	7185	41.34	40.45	39.26
7384	7432	44.51	43.91	42.63
7613	7662	47.50	46.86	45.51
7794	7846	49.88	49.19	47.75
7798	7866	50.14	49.25	47.81
8011	8061	52.64	51.95	50.43
8240	8290	55.56	54.94	53.34
8494	8544	58.84	58.23	56.53
8740	8812	62.32	61.38	59.60
9100	9145	66.62	66.05	64.10
9472	9518	71.42	70.83	68.74
9900	9946	76.96	76.33	74.10
10418	10453	83.46	83.01	80.60
11047	10959	90.03	91.15	88.46
11735		100.00	100.00	97.00

In a second series the solutions used were weighed instead of being measured :

Table II.

$10^6 \times k_{obs.}$	$10^6 \times k_{calc.}$	Per cent acid used.	Per cent acid found. (Equation 5'.)	Per cent acid found. ($\mu = 383$.)
3995		0.00	0.00	0.00
4067	4087	1.19	0.93	0.90
4434	4480	6.27	5.66	5.50
4918	4944	12.33	11.97	11.71
5259	5311	16.97	16.30	15.85
5814	5856	24.01	23.44	22.95
6681	6723	35.18	34.64	33.68
7178	7216	41.46	40.92	40.05
8020	8048	52.25	51.91	50.48
9125	9132	66.25	66.17	64.33
10619	10603	85.20	85.44	83.07
11748		100.00	100.00	

In a last series solutions of varying normality, from N/16 to
N/32, were employed. They were prepared from a solution
that was N/16 in regard to the acid as well as the salt (50 cc.
N/16 hydrochloric acid was mixed with 50 cc. N/16 potassium
chloride solution), and that was diluted systematically in a
first series with N/32 hydrochloric acid, in a second series with
the corresponding solution of potassium chloride. The re-
sulting solutions were treated as isohydric mixtures of acid
and salt of an easily ascertained normality. For instance, the
solution obtained by the removal of 50 cc. of the original mix-
ture and the addition of 50 cc. N/32 potassium chloride con-
tained 1/64 gram-molecule acid and 2/64 gram-molecule salt
per liter, or a total of 3/64 gram-molecule electrolyte. It was
therefore N/21.33 as regards the total electrolyte content, and
a mixture of one-volume (33.3 cc.) of N/21.33 acid and two
volumes (66.7 cc.) of N/21.33 salt. These equimolecular
solutions being considered isohydric, the amount of free acid
could be ascertained according to equation (5) by a measure-
ment of the conductivity of the solution. The molecular con-
ductivities of the salt and acid for these concentrations were
readily found by interpolation from the values for N/16 and
N/32 solutions. The latter values were determined for the
solutions of acid and salt actually employed. Table III.

gives all the results : Column 1 gives the volume, in liters, containing 1 gram-molecule total electrolyte ; the other columns have the same significance as in the previous tables.

Table III.

$v.$	$10^6 \times k_{obs}.$	Per cent acid used.	Per cent acid found. (Equation 5.)
16.0	7741	0.00	
32.0	3990	0.00	
16.0	22960	100.00	
32.0	11720	100.00	
31.75	4078	0.78	0.73
31.51	4155	1.54	1.31
31.03	4326	3.33	2.67
30.12	4692	5.88	5.61
28.44	5399	11.11	10.67
25.60	6830	20.00	19.54
21.33	9693	33.33	32.98
16.0	15374	50.00	50.16
16.0	15380	50.00	50.19
21.33	13620	66.67	67.10
25.60	12691	80.00	80.43
28.44	12241	88.89	89.50
30.12	12011	94.12	94.82
31.03	11924	96.67	98.06

Aniline Hydrochloride and Hydrochloric Acid.

With the aid of the expression developed in equation (5), a study was also made of the conditions of equilibrium in solutions of aniline hydrochloride in which the proportions of the base and acid were varied in such a way that a greater or less excess of acid was used beyond that required for salt formation. The solutions were always made of $N/32$ strength as regards the aniline hydrochloride, except in the last case recorded in the table, in which a $N/64$ solution of the salt was employed. By the use of an excess of acid they became more concentrated in regard to the total content of electrolyte and for the calculation the molecular conductivities, M_v, μ_v, and $\mu_{HCl(v)}$, were used always with reference to the volume containing 1 gram-molecule total electrolyte as explained below.

In Table IV. the first column gives the volume in liters

containing 1 gram-molecule electrolyte; in the second column the observed molecular conductivity is given. Column 3 brings the acid found in percentages of the total electrolyte present, as calculated by means of equation (5) from the observed molecular conductivities M_v and the molecular conductivities $\mu_{HCl(v)}$ of hydrochloric acid, and μ_v of the non-hydrolyzed salt for the total concentration of the electrolyte used. These conductivities were obtained by interpolation from the values for μ_{16} and μ_{32} (88.1 and 92.1) for non-hydrolyzed aniline hydrochloride,[1] and $\mu_{HCl(16)}$ and $\mu_{HCl(32)}$ (367 and 376.4) for hydrochloric acid as determined by us for the acid actually used. For instance, in the second experiment recorded in the table 1 liter of the solution contained 1/32 or 16/512 gram-molecule aniline hydrochloride and 1/512 gram-molecule excess of added acid, a total of 17/512 gram-molecule electrolyte, or 1 gram-molecule in 30.12 liters. The observed specific conductivity was 0.003702, the observed molecular conductivity, therefore:

$$M_v = 0.003702 \times 30.12 \times 1000$$
$$= 111.5$$

$\mu_{30.12}$ for aniline hydrochloride (non-hydrolyzed), is 91.8, $\mu_{HCl(30.12)}$ for hydrochloric acid is 375.4. If x represents the percentage of free acid in parts of total electrolyte, we have by substitution of these values in (5):

$$x = \frac{111.5 - 91.8}{375.4 - 91.8}$$
$$= 0.0695$$

As the excess of acid added was 1/17 or 5.88 per cent of the total electrolyte present, 1.07 per cent of acid must have been formed by hydrolysis of the aniline salt. For comparison with these results found experimentally, as just described and given in column 3, the next column brings the theoretical amount of acid in percentages of total electrolyte, which should be present according to the known affinity constant of aniline. The theoretical figures are ascertained as follows:

[1] *Vide* Bredig: Ztschr. phys. Chem., **13**, 215, 322 (1894).

For the condition of equilibrium in a hydrolyzed solution of aniline hydrochloride (see equation 1), we have :[1]

$$C_s = K \times C_b \times C_a, \tag{6}$$

in which C_s, C_b, C_a express the gram-molecules of non-hydrolyzed salt, free base, and free acid in 1 liter of the solution. K is the constant ratio[2] between the affinity constant of aniline and the degree of dissociation of water (1.2×10^{-14}), and has a known value.[3]

The application of equation (6) to the calculation of the theoretical amount of acid which should be present in our experiments will be illustrated by the calculation of the value for the second experiment in the table. As explained above in this experiment, 1 liter of the solution was made to contain 1/32 gram-molecule aniline hydrochloride and 1/512 gram-molecule excess of acid, 1 gram-molecule total electrolyte being contained in 30.12 liters, a volume which may be designated by V. The excess of acid used was 1/17 or 5.88 per cent, and if we call y the percentage of additional acid formed by hydrolysis of the salt, then the total concentration of free acid was $(0.0588 + y) : V$. The concentration of the free base was $y : V$, of the non-hydrolyzed salt $(0.9412 - y) : V$. Substituting the values in (6), we obtain :

$$30.12\ (0.9412 - y) = 40{,}000 y\ (0.0588 - y).$$

Solving for y, we find y is 0.0102 and the total free acid therefore 5.88 and 1.02, or 6.90 per cent of the total electrolyte. The theoretical amount of free acid is then 6.90 per cent ; the amount found above, by means of a conductivity measurement and equation (4), was 6.95 per cent.

The last column of the table gives the excess of acid used, in percentage of the total electrolyte present.

[1] Walker : Ztschr. phys. Chem., **4**, 319 (1889).

[2] Arrhenius : *Ibid.*, **5**, 16 (1890).

[3] K was taken to be 40,000, the mean between Bredig's value (41,000) and the constant (39,000) calculated from Bredig's data by means of equation (5).

Table IV.

$v.$	$M_v.$	Per cent acid found.	Per cent acid, theory.	Excess acid, used.
31.03	105.7	4.83	4.56	3.03
30.12	111.5	6.95	6.90	5.88
28.44	124.1	11.47	11.53	11.11
28.44	124.3	11.56	11.53	11.11
25.60	147.8	20.06	20.26	20.00
21.33	183.2	33.11	33.48	33.33
16.00	227.5	49.92	50.08	50.00
16.00	227.7	50.01	50.08	50.00
21.33	278.5	66.97	66.80	66.67

The results given in Tables I. to IV. show that Walker's interpretation of μ_{HCl}, in his fundamental equation as the molecular conductivity of hydrochloric acid referred to the total electrolyte content, gives the closest approximation to the true values for the free acid, and the equation should be used in that sense in the analysis of hydrolyzed solutions by the conductivity method. Although there are more accurate methods of analysis of such solutions, this is the most rapid one and it may be used successfully in the case of solutions undergoing continuous change. An illustration of an application to the determination of the velocities of such changes and of the affinity constants of unstable weak bases will be brought in the next report on the rearrangement velocities and affinity constants of aminophenyl alkyl carbonates.

CHICAGO, January, 1904.

THE MOLECULAR REARRANGEMENT OF AMINO-PHENYL ALKYL CARBONATES.[1]

BY J. STIEGLITZ AND HENRY T. UPSON.

When *o*-nitrophenyl ethyl carbonate is reduced with tin and hydrochloric acid without any special precautions, an alkali-soluble body is obtained[2] in place of the amine which aro-

[1] The experimental work described in this paper was carried out by Mr. Upson under my direction. I am glad to take this occasion to acknowledge the valuable assistance of my collaborator. He is not responsible for the theoretical treatment of the material. J. STIEGLITZ.

[2] Bender: Ber. d. chem. Ges., **19**, 2268 (1886); H. N. McCoy: This JOURNAL, **21**, 111 (1899).

matic nitro compounds usually give under such treatment.
J. H. Ransom,[1] working under the direction of one of us,
showed that the formation of the acid body, oxyphenyl-
urethane, is due to a molecular rearrangement of the
primary product of the reduction, *o*-aminophenyl ethyl car-
bonate. The rearrangement proceeds according to

$$H_2NC_6H_4OCO_2C_2H_5 \rightarrow C_2H_5O_2C.NH.C_6H_4OH,$$
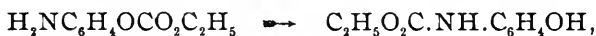
the carbethoxyl group leaving the negative phenol group and
going to the basic amino radical. Working under special
conditions, Ransom was able to isolate and study both the
free base itself and its hydrochloride. The free base was
found to go over spontaneously, in the course of several hours,
into the isomeric oxyphenylurethane ; the hydrochloride,
however, was found to be perfectly stable in a dry condition,
but in aqueous solution it was also gradually converted into
oxyphenylurethane, hydrochloric acid being liberated at the
same time.

Similar migrations of acyl radicals to neighboring amine
groups have been observed both before and after the investi-
gation of Ransom, but the interesting intermediate product,
the amine, was isolated only in the one case studied in this
laboratory. The present work was carried out with the view
to ascertaining to what extent the tendency to rearrange ex-
ists in the case of substitution-products of *o*-aminophenyl ethyl
carbonate, and to what extent the amines or their salts can be
isolated as intermediate products ; more especially, however,
it was decided to determine the velocity of the rearrangement
and the factors on which the latter depends. Regarding the
first two objects, it was found that all twelve of the *o*-amino-
phenyl carbonates investigated show the tendency to rear-
rangement into urethanes, and that in every single case the
hydrochloride of an amine could be isolated, even when the
velocity of rearrangement under ordinary conditions is an ex-
tremely high one. The results of this portion of the investi-
gation will be found in a later paper by one of us,[2] while parts
I. and II. of this paper will deal with the work on the velocity

[1] This JOURNAL, **23,** I (1900).
[2] Upson : See a later number of this JOURNAL.

of the rearrangement of these bodies when their hydrochlorides are dissolved in water or in dilute alcohol.

PART I.

Aminophenyl alkyl carbonates may be regarded as substituted anilines ; like aniline, they can be but weak bases, and it was expected that they would prove to be weaker bases than aniline—an expectation which was verified by experiment.   In an aqueous solution of the hydrochloride of such a base, hydrolytic dissociation must ensue and a condition of equilibrium be established according to the well-known equation :

$$RO_2COC_6H_4NH_3Cl + H_2O \; \rightleftarrows$$
$$RO_2COC_6H_4NH_3OH + HCl. \quad (1)$$

Representing the concentrations of the salt, free base, and free acid by C_s, C_b, and C_a, respectively, the condition of equilibrium is expressed according to Walker[1] by the equation

$$C_s = KC_bC_a. \quad (2)$$

K is a constant and represents the ratio[2] between the affinity constant, K_b, of the base and the dissociation constant[3] of water, K_{H_2O}, so that we have

$$\frac{C_s}{C_b \cdot C_a} \;=\; \frac{K_b}{K_{H_2O}}. \quad (2')$$

The reaction according to which an aminophenyl alkyl carbonate is rearranged would be non-reversible, and it could involve both the salt (or its positive ion) and the free base, and be represented by

$$RO_2COC_6H_4NH_3Cl \; \rightarrow \; HOC_6H_4NHCO_2R + HCl, \quad (3)$$

and

$$RO_2COC_6H_4NH_3OH \; \rightarrow \; HOC_6H_4NHCO_2R + H_2O. \quad (4)$$
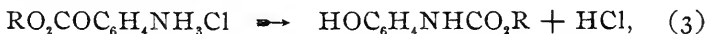
If only the free base in the solution were capable of rearrangement, the reaction would be expressed by (4) or by the closely related equation,

[1] Ztschr. phys. Chem., **4**, 319 (1889).
[2] Arrhenius : *Ibid.*, **5**, 17 (1890).
[3] 1.2 × 10⁻¹⁴. Van 't Hoff's "Lectures on Theoretical Chemistry," p. 133.

$$RO_2COC_6H_4NH_2 \quad \rightleftharpoons \quad HOC_6H_4NHCO_2R. \qquad (5)$$
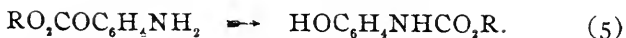
It was suspected at once that the rearrangement proceeds wholly by the rearrangement of the free base (4) or (5) : the stability of the dry hydrochlorides, the spontaneous rearrangement of the isolated free base, *o*-aminophenyl ethyl carbonate, and the delay in rearrangement when an excess of hydrochloric acid is added to the aqueous solution, all pointed plainly to such a conclusion. From equations (1) and (2), namely, it follows that in the presence of an excess of acid the concentration of the free base must be reduced. Now from equations (1) and (4) or (5) it would also follow that as the rearrangement reaction proceeded free hydrochloric acid would accumulate and act as a check on the further rearrangement— changing the rate of change of the total substance present, but not affecting the rate of change of the free base present, provided the rearrangement proceeds only according to equation (4) or (5). ·

Hydrochloric acid, which as a catalyzer is found to increase so greatly the velocity of many reactions, would then by a simple chemical action—salt formation—affect the velocity in this case negatively, and it was the idea of testing this view quantitatively that proved the greatest incentive to undertake the investigation.

At the same time it was thought desirable to ascertain whether the tendency to rearrange, as shown by the velocity constants, is augmented by an increase in the positive character of the amino group, as determined by the affinity constants of the bases examined. By such an increase the basic group might or might not exert a more powerful attraction on the neighboring negative carbethoxyl group. Finally, it was hoped to detect the effect of stereochemical influences on the reaction, if any exist.

If the two substances holding the carbethoxyl group in favorable proximity to the amine group for a migration, namely the salt and the base, rearrange with equal velocity, then for a monomolecular reaction (3) or (4) we would have

$$\frac{dx}{dt} = k(C-x), \tag{6}$$

and

$$k = \frac{1}{t}\log. \text{ nat.}\frac{C}{C-x}, \tag{6'}$$

where k would be a constant, representing the reaction-velocity, and C the total concentration of substance, salt, and base, originally present, and x the amount changed in time t. If, on the other hand, only the free base existing in the hydrolyzed solution of the salt undergoes rearrangement, we would have

$$\frac{dx}{dt} = kC_b. \tag{7}$$

But C_b is, in turn, according to (2), dependent on the concentration of the free acid formed by hydrolysis and liberated by the rearrangement.

The dependence of C_b on the progress of the rearrangement can be expressed as follows, according to the two simultaneous reactions, the non-reversible one of transformation,

$$RO_2CO.C_6H_4NH_2 \quad \longrightarrow \quad HOC_6H_4NHCO_2R, \tag{5}$$

and the reversible hydrolytic reaction,

$$RO_2COC_6H_4NH_3Cl + H_2O \rightleftarrows$$
$$RO_2COC_6H_4NH_3OH + HCl. \tag{1}$$

The total concentration of the substance used may be called 1 gram-molecule in a definite volume V (*e. g.*, 32 liters). We will let y represent the concentration of the free base at any time, t, in terms of parts of the gram-molecule in the volume V, and x represent, in the same terms, the parts of the gram-molecule rearranged to the urethane in time t. Then the concentration of the salt at the moment, t, is equal to $1-(x+y)$ gram-molecules in V liters as the total organic matter is present either as salt, base or urethane ; and finally $(x+y)$ represents the concentration of the free acid at any moment, t, in gram-molecules in V liters. Equation (2) becomes then :

$$\frac{1-(x+y)}{V} = K\frac{(x+y)y}{V^2},$$

or
$$\frac{1-(x+y)}{(x+y)y} = \frac{K}{V}. \tag{8}$$

For a given constant volume (*e. g.*, $V = 32$), we have

$$(K : V) = K_1,$$

and
$$\frac{1-(x+y)}{(x+y)y} = K_1. \tag{8}'$$

Solving for y, we have

$$y = \frac{-(K_1 x + 1) + \sqrt{(K_1 x + 1)^2 - 4K_1 (x-1)}}{2K_1}; \tag{9}$$

$\frac{y}{v}$ is the C_b and $\frac{x}{v}$ the x of equation (7) and substituting these values in (7), we have

$$\frac{d\frac{x}{v}}{dt} = k\frac{y}{v} \quad \text{or} \quad \frac{dx}{dt} = ky. \tag{10}$$

Introducing the value found for y in (9), we obtain from (10):

$$kt = 2K_1 \int \frac{dx}{-(K_1 x + 1) + \sqrt{(K_1 x + 1)^2 - 4K_1 (x-1)}}, \tag{11}$$

or
$$kt = \int \frac{dx}{y}.$$

If we call y_t the concentration of the base in parts of a gram-molecule in V liters, as determined according to (9) at the time t, and y_0 its concentration when $t = 0$ and $x = 0$, we have by integrating (11):[1]

$$kt = \frac{-K_1}{1 + K_1 y_t} + K_1 \log. \text{nat.} \left(K_1 + \frac{1}{y_t}\right) - \log. \text{nat.} y_t$$

$$+ \left[\frac{K_1}{1 + K_1 y_0} - K_1 \log. \text{nat.} \left(K_1 + \frac{1}{y_0}\right) + \log. \text{nat.} y_0\right]. \tag{12}$$

The equations (12) and $(6')$ show, therefore, how the speed of the reaction would be affected by the question whether the

substance undergoing rearrangement is simply the free base present by hydrolysis, or the free base and salt indifferently, and would enable us to decide this question if the necessary analytical data could be obtained.

In order to answer the question experimentally it was necessary, therefore, to determine, on the one hand, the affinity constant of equation (8), and, on the other hand, to ascertain, for any moment, the concentration of the free base (y_t) and the amount of rearrangement (x), as used in equations (9) and (12).

It may be stated at once that for the aminophenyl carbonates examined quantitatively, equation (12) was found to give the correct course of the reaction ; perfectly satisfactory velocity constants are obtained from the experimental data by this equation (12), while the application of the ordinary formula for monomolecular reactions, (6), led to no constants. We have, therefore, a monomolecular rearrangement of the free base formed by hydrolysis, proceeding all the time according to the monomolecular equation at a rate of change proportionate to the free base present at any moment ; simultaneously the free acid accumulating by the rearrangement suppresses the free base and retards the apparent rate of change, but it does not affect the real rate of change as referred to the concentration of the base. The experimental study of the two simultaneous reactions was a matter of considerable difficulty, but also of great interest. The methods used will now be described.

Determination of the Affinity Constants.

Of the various methods[1] for determining the affinity constants of bases, K, as used in (8), all but one were impossible of application, owing to the very rapid change in the condition of equilibrium between the base, salt, and acid, produced by the rapid rate of rearrangement. For instance, the very accurate method of determining the amount of free acid in a

[1] Warder : This JOURNAL, **3,** 340 (1882) ; Ostwald : J. prakt. Chem., **35,** 112 (1887) ; Will : Ber. d. chem. Ges., **21,** 2777 (1888) ; Reicher : Ann. Chem. (Liebig), **228,** 257 (1885) ; Walker : Ztschr. phys. Chem., **4,** 319 (1889) ; Bredig : *Ibid.,* **13,** 288 (1894) ; Loewenherz : *Ibid.,* **25,** 385 (1898) ; Farmer : J. Chem. Soc. (London), **79,** 863 (1901).

hydrolyzed solution of the salt of a weak base and a strong acid by catalytic decomposition of methyl acetate[1] could obviously not be applied in this case. A method allowing of nearly instantaneous results was necessary, and such a method is the conductivity method of Walker[2] and Bredig[3]. It promised the most feasible process of analysis and was therefore employed. In a solution in which a condition of equilibrium exists between a strong acid and a weak base, their salt and water, according to (1), the conductivity for a given temperature depends wholly on the amounts and concentrations of the salt and the free strong acid present.[4]

If we call the total concentration 1 gram-molecule in V liters, and the amount of free acid present p gram-molecules in V liters, then the concentration of the base is also p gram-molecules and that of the salt $(1 - p)$ gram-molecules in V liters. According to the formula established in the preceding paper[5] we have then :

$$M_v = (1 - p)\mu_v + p\mu_{\text{HCl}(v)}, \qquad (13)$$

where M_v represents the observed molecular conductivity and μ_v the molecular conductivity of the non-hydrolyzed salt and $\mu_{\text{HCl}(v)}$ the molecular conductivity of the free hydrochloric acid, all at the same volume V (see the previous paper). Then

$$p = \frac{M_v - \mu_v}{\mu_{\text{HCl}(v)} - \mu_v}, \qquad (14)$$

and according to (2′) :

$$\frac{V(1 - p)}{p^2} = K = \frac{K_b}{K_{\text{H}_2\text{O}}}. \qquad (15)$$

In order to apply equation (14) it was necessary to determine the molecular conductivity, μ_v, of the non-hydrolyzed salt at the temperature used. Bredig's method of determining μ_v directly by suppressing the free acid by means of an

[1] Walker : *Loc. cit.*
[2] Ztschr. phys. Chem., **4,** 333 (1889).
[3] *Loc. cit.*
[4] Walker : *Loc. cit.*
[5] Stieglitz and Derby : This JOURNAL, **31,** 449 (1904).

excess of the free base[1] was tried, but it proved a failure partly on account of the difficult solubility of the free *o*-aminophenyl ethyl carbonate, which refused to neutralize all the free acid, and partly on account of the continuous rapid formation of free acid by the rearrangement reaction. In applying the above equation, (14), μ_v is also very generally ascertained by comparison of the base under investigation with a base, similar in composition and the number of atoms contained in the molecule, for whose hydrochloride Bredig or others have determined the molecular conductivities. The molecular conductivity of the salt under investigation is simply made equal to the molecular conductivity of the corresponding salt of the nearest similar base. Even this method was not directly applicable ; the rapid rate of rearrangement made it necessary to work at $0°$, and the conductivities of few salts of organic bases seem to have been determined at $0°$.

The reduction of the molecular conductivities of the hydrochlorides of the nearest similar bases as determined at $25°$ by Bredig to $0°$, by means of temperature coefficients calculated by us from the careful work of Jones[2] on the conductivity of a number of inorganic salts at $0°$, gave results which were entirely incompatible with the observations. For instance, the hydrochlorides of *p*-aminophenyl ethyl and methyl carbonates, which do not rearrange, and for which M_v can be determined very accurately, gave no constants[3] on applying the general equations (14) and (15) with the help of molecular conductivities reduced to $0°$ from Bredig's figures for $25°$ for bases of analogous composition.[4] For the former base we found for K 266400 $(v = 32)$; 121000 $(v = 64)$; 63000 $(v = 128)$; etc.

A solution of the difficulty was found and the values for the molecular conductivities of the hydrochloride of *o*-aminophenyl ethyl carbonate ascertained by a determination of the molecular conductivities of the hydrochloride of the isomeric *p*-aminophenyl ethyl carbonate and by our putting those of

[1] *Loc. cit.*, p. 214.

[2] This JOURNAL, **26**, 428 (1901).

[3] All of our results indicate that the temperature coefficients for salts of complex organic bases will be found a little larger than those determined by Jones for simple inorganic salts.

[4] Bredig ; Ztschr. phys. Chem., **4**, 216 (1889).

the hydrochloride of the ortho base equal to these same con-
ductivities. The hydrolyzed solution of the hydrochloride of
the para base is very stable in aqueous solution and permits
of very accurate determinations of the observed conductivi-
ties ; and as isomers of this kind have practically identical
molecular conductivities, it was sufficient to determine these
for the stable isomer.

The Affinity Constant of p-Aminophenyl Ethyl Carbonate and the Molecular Conductivities of Its Hydrochloride.

The molecular conductivities of the non-hydrolyzed hydro-
chloride of p-aminophenyl ethyl carbonate were ascertained as
follows : According to equation (15) we have for the aqueous
hydrolyzed solution of the salt

$$\frac{v(1-p)}{p^2} = K.$$

For a second solution containing 1 gram-molecule of the salt
in v_1 liters, we have

$$\frac{v_1(1-p_1)}{p_1^2} = K,$$

and therefore

$$\frac{v(1-p)}{p^2} = \frac{v_1(1-p_1)}{p_1^2} \quad \text{and} \quad \frac{p^2}{p_1^2} = \frac{v}{v_1} \cdot \frac{1-p}{1-p_1}. \quad (16)$$

Dropping for the present $(1-p) : (1-p_1)$ as nearly equal to
unity for a first approximation, and making $v = 32$ and $v_1 =
128$, we obtain

$$p_{32} = 0.5\, p_{128}. \quad (17)$$

p_{32} being put equal to $0.5\, p_{128}$, a preliminary calculation of μ_{32}
and μ_{128} was made by the same method as will be used pres-
ently for the final exact calculations (see equations (19), (20),
(21), and (22)), and from the found approximate values of μ_{32}
and μ_{128}, p_{32} and p_{128} were ascertained as first approximations
by (14) and found as follows :

$$p_{32} = 0.04 \qquad \text{and} \qquad p_{128} = 0.08.$$

Inserting these values in (16) we have more accurately :

$$\frac{p_{32}^2}{p_{128}^2} = \frac{1}{4} \times \frac{1-0.04}{1-0.08}$$
$$= \frac{1}{4} \times 1.04,[1]$$

and therefore

$$p_{32} = 0.51 \, p_{128}. \tag{18}$$

μ_{32} was then finally calculated as follows :   According to (14)

$$p_{32} = \frac{M_{32} - \mu_{32}}{\mu_{32(HCl)} - \mu_{32}}.$$

The observed molecular conductivity[2] M_v when v is 32 at $o°$, was 51.1, and the molecular conductivity of hydrochloric acid at $o°$ when v is 32 is 233.6.[3]   Therefore

$$p_{32} = \frac{51.1 - \mu_{32}}{233.6 - \mu_{32}}. \tag{19}$$

In the same way

$$p_{128} = \frac{M_{128} - \mu_{128}}{\mu_{128(HCl)} - \mu_{128}}. \tag{20}$$

The differences between molecular conductivities at these dilutions are rather small and constant values, which are used, in fact, as constants at $25°$.[4]

The value of this constant at $o°$ for $\mu_{128} - \mu_{32}$, ($\varDelta$ 128, 32), was taken as 2.7[5] as the average of all the values calculated by us from Jones' results at $o°$.   Introducing into (20) this

[1] For the corrected values of p_{32} and p_{128} (0.038 and 0.075), $(1-p) : (1-p_1)$ is 1.039; the value used above, 1.04, needs therefore no second correction.

[2] The method used in determining all the conductivities given in this paper was that of Kohlrausch, involving the use of a Wheatstone bridge and a telephone. The conductivities are given in reciprocal mercury units. A constant temperature of $o°$ was maintained by means of melting ice. The hydrochlorides of the aminophenyl alkyl carbonates are very soluble in water. Even at $o°$ the solution takes place almost instantly. This temperature was used beeause at higher temperatures the rearrangement of the bases of the ortho series is so fast that satisfactory reading with the telephone could not be made. A Kohlrausch cell was used and in measuring the velocity of rearrangements by changes in conductivities, the electrodes were frequently removed from the solution and washed with pure alcohol and ether to remove any adhering deposit of an oxyphenylurethane, the insoluble product of the rearrangement.

[3] Jones : *Loc. cit.* Exactly the same value was also found by us.

[4] *Vide* Bredig : Ztschr. phys. Chem., **4**, 198 (1889) ; and Ley : *Ibid.*, **30**, 234 (1899).

[5] It is also close to the value found for the constant (about 3) calculated from Bredig's Δ 128, 32 for $25°$ by means of the temperature correction. (*Vide* footnote.)

value as well as the found values for M_{128} and $\mu_{128(HCl)}$[1] we obtain

$$p_{128} = \frac{61.0 - (\mu_{32} + 2.7)}{239.0 - (\mu_{32} + 2.7)}, \tag{21}$$

$$p_{128} = \frac{58.3 - \mu_{32}}{236.3 - \mu_{32}}, \tag{21'}$$

from (18), (19), and (21)

$$\frac{51.1 - \mu_{32}}{233.6 - \mu_{32}} = 0.51 \frac{58.3 - \mu_{32}}{236.3 - \mu_{32}}. \tag{22}$$

Solving for μ_{32}, we find $\mu_{32} = 43.8$.

Then μ_{128} is 46.5. As Δ 64, 32 may be put equal to 0.5 Δ 128, $32^2 \mu_{64}$ is 45.15. Δ 512, 128 is calculated by us as 1.7[3] as the average of all of Jones' results and Δ 256, 128 is 0.5 Δ 512, 128. We have then for μ_{256} 47.4.[4]

Using these values to determine the hydrolysis constant K for p-aminophenyl ethyl carbonate, according to (14) and (15), we obtain the following results :

$v.$	$M_v.$		$\mu_v.$	$100p.$		K.	
	I.	II.		I.	II.	I.	II.
32	51.0	51.19	43.8	3.79	3.89	21400	20300
64	54.94	55.20	45.15	5.11	5.25	23200	22000
128	61.09	60.90	46.5	7.58	7.48	20600	21100
256	66.33	66.33	47.4	9.82	9.82	23900	23900
						Mean,	K = 22000

The agreement among the values for K is quite satisfactory, which shows that the molecular conductivities as determined are sufficiently accurate. K for aniline was found by Bredig as 41000. All of these values of K mean that in accordance with equation (2) the base under investigation has an affinity constant K times as great as the dissociation constant of water, which is 1.2×10^{-14}.

[1] Jones : *Loc. cit.*

[2] See Bredig's table for 25°. Ztschr. phys. Chem., **4**, 198 (1889).

[3] It is also close to the value (2) calculated from Bredig's Δ 512, 128, (4), at 25° by means of a temperature correction.

[4] Small errors in the determination of μ_v do not affect the values of the affinity constants very much, as μ_{HCl} and M_v are very much larger than μ_v in (16).

The Affinity Constant of p-Aminophenyl Methyl Carbonate and the Molecular Conductivities of Its Hydrochloride.

The same methods were applied to the determination of the molecular conductivities of the hydrochloride of p aminophenyl methyl carbonate, $NH_2C_6H_4OCO_2CH_3$, and to the determination of the affinity constant of the base. It was again found that

$$p_{32} = 0.51 \ p_{128}. \tag{23}$$

In the equation developed from this relation

$$\frac{M_{32} - \mu_{32}}{\mu_{HCl(32)} - \mu_{32}} = \frac{0.51 \ [M_{128} - (\mu_{32} + 2.7)]}{\mu_{(HCl)_{128}} - (\mu_{32} + 2.7)}, \tag{24}$$

μ_{32} is the only unknown. Introducing the known and observed values we have

$$\frac{52.8 - \mu_{32}}{233.6 - \mu_{32}} = \frac{0.51 \ [62.4 - (\mu_{32} + 2.7)]}{239.0 - (\mu_{32} + 2.7)},$$

and solving for μ_{32}, we find

$$\mu_{32} = 45.9.$$

μ_{641}, μ_{128}, and μ_{256} were determined as above for the homologous base. The results obtained are given in the following table:

v.	M_v.	μ_v.	$100p$.	K.
32	52.77	45.9	3.68	22800
64	57.33	47.25	5.33	21300
128	62.42	48.6	7.25	22600
256	67.53	49.5	9.45	25900
			Mean,	23200

The agreement in the values of K is satisfactory.

The Affinity Constants of o-Aminophenyl Alkyl Carbonates.

The molecular conductivities of the non-hydrolyzed hydrochlorides of the p-aminophenyl alkyl carbonates having been determined, those of the hydrochlorides of the isomeric ortho bodies, the bases under investigation, may without hesitation

be taken as equal to them at the same temperature. The hy-
drochlorides of the three isomeric toluidines show nearly iden-
tical molecular conductivities at 25°, and at 0° the differences
would be reduced to half, or even less than half, the differ-
ences at 25°.[1] From these known values of the molecular
conductivities, μ_v, of the hydrochlorides of o-aminophenyl alkyl
carbonates, the observed molecular conductivities, M_v, and
the known molecular conductivity of hydrochloric acid at 0°,
the affinity constants of the bases of the ortho series may be
estimated according to the equations (14) and (15).

In the observed molecular conductivities, M_v, there is, how-
ever, a small error due to the fact that in the one or two min-
utes required to dissolve the salt in the required volume of
water and to determine the conductivity with the apparatus
of Kohlrausch the molecular rearrangement releases some
free hydrochloric acid (equations (1) and (4)), and increases
therefore the observed molecular conductivity and the appar-
ent degree of hydrolysis a small amount, as calculated ac-
cording to (14). The values of the hydrolysis constant K will
consequently be found somewhat too small. In order to
eliminate this not very considerable error a first approximate
estimation of the degree of hydrolysis (p) and the affinity
constant, K, was made according to (14) and (15) from the
first values observed at the end of from one to two minutes.
With the aid of these first approximate values, the velocity of
rearrangement was estimated approximately but with consider-
able accuracy by the same methods that will be described be-
low for the final calculation of the velocity.

The amount of rearrangement in the carefully timed inter-
val between the first reading and the first moment when water
touched the salts (one to two minutes) was then estimated
with the aid of the approximate velocity constants, and in this
way the condition of the solution, when t is 0, determined
with sufficient accuracy. The experimental data for the hy-
drochloride of o-aminophenyl ethyl carbonate will serve to il-
lustrate the method.

In equation (14) the specific conductivities at the dilutions
[1] Bredig : *Loc. cit.*, p. 216.

used and at o°, k_{obs}, k_v, $k_{v(HCl)}$, may be substituted for the molecular conductivities ; as specific conductivities were found first and a great many readings were made in determining the velocities, we found it often much more convenient to use the following formula in place of equation (14) for calculating the degree of hydrolysis(p) :

$$p = \frac{k_{obs} - k_v}{k_{v(HCl)} - k_v}.^{1}$$ (25)

The data for the approximate calculation of the degree of hydrolysis, p, of the hydrochloride of o-aminophenyl ethyl carbonate and of the affinity constant of the base, (equation (15)), are given in the following table. In the first column we have the volumes containing 1 gram-molecule of the substance ; in the second the observed specific conductivities at o° ; in the third the specific conductivities of the non-hydrolyzed salts at o° as calculated from the molecular conductivities (p. 469) ; in the fourth column the specific conductivities of hydrochloric acid at o° according to Jones ; in the fifth column the degree of hydrolysis ; and in the last column the calculated affinity constant :

Table I.

v.	$10^6 \times k_{obs}$.		$10^6 \, k_{salt}$.	$10^6 \, k_{acid}$.	$100 \, p$.		K.	
	I.	II.			I.	II.	I.	II.
32	2488	2488	1369	7300	18.9	18.9	730	730
64	1472	....	706.3	3700	25.6	...	730	...
128	876.2	836.5	363.3	1867	34.1	31.5	725	885
256	505.1	505.4	185.1	937	42.5	42.5	810	810
						Mean,	K = 775	

The agreement, under the conditions used, is satisfactory.

As was stated above, and will be shown below, the rate of rearrangement is proportional to the concentration of the base present at any moment, a constant being found according to the equations (7) and (12). The following table, II., gives the data for the preliminary estimation of this velocity

---

[1] k_{obs} is the observed specific conductivity of the hydrolyzed solution of the salt, k_v the specific conductivity of the non-hydrolyzed salt, $k_{v(HCl)}$ that of hydrochloric acid, all for solutions of 1 gram-molecule of the substance in v liters.

constant which will be used for correcting the values just given for the time that elapsed between the first moment of solution and the first reading of the conductivity.

The concentration used was 1 gram-molecule of the hydrochloride in 32 liters. All the concentrations in the table are given as parts (per cent) of this gram-molecule in 32 liters. Column 1 gives the time in minutes ; column 2 gives the free acid, p_t, present at any moment, t; the method of analysis by means of which this amount of free acid was ascertained (by conductivity measurements) for any moment will be described in detail below. The salt, s_t, (column 3) is always equal to $(1 - p_t)$ according to equation (1), and the free base b_t (column 4) is then calculated by equation (2) by insertion of the values for C_s and C_a and $K(775)$; x, the amount rearranged in time t, is equal to $(1 - s_t - b_t)$ or $(p_t - b_t)$, (column 5). The approximate velocity constant, k, was calculated according to

$$k(t - 2) = - \frac{K_1}{1 + K_1 b_t} + K_1 \log. \text{nat.} \left(K_1 + \frac{1}{b_t}\right) - \log. \text{nat.} b_t$$

$$+ \left[\frac{K_1}{1 + K_1 b_2} - K_1 \log. \text{nat.} \left(K_1 + \frac{1}{b_2}\right) + \log. \text{nat.} b_2\right], \quad (26)$$

which is derived from equation (12) by taking the time for the first reading of the conductivity, *viz.*, two minutes after the solution was made, as the starting-point for the calculation ; b_2 is the concentration of the base at that moment. The constant expression in equation (26), which is bracketed, has the value —79.435, and K_1 is $K : V$ or $775 : 32$.

Table II.

t.	$100p_t$.	$100s_t$.	$100b_t$.	$100x$.	k.
2	18.9	81.1	17.7	21.16	0.056
30	30.55	69.45	9.36	25.58	0.055
40	33.7	66.3	8.12	34.95	0.059
60	40.9	59.1	5.95	40.55	0.057
80	45.5	54.5	4.95	45.85	0.057
120	53.1	46.9	3.65	49.45	0.056
150	58.3	41.7	2.95	55.35	0.057

Mean, $k = 0.056$

In the following table, III., we now give the data of Table
I. as corrected with the aid of the velocity constant, k, for the
time that elapsed between the first moment of solution ($t = 0$)
and the first readings of the conductivities.   Column 1 gives
the volumes containing 1 gram-molecule of the substance ;
columns 2 and 3 give the calculated concentration of the free
acid (p_0) and free base (b_0) when t is 0 ; this concentration
must satisfy the velocity constant ($k = 0.056$) for the small
time interval (t_1) and is found by successive substitution of
values smaller than the degree of hydrolysis (p) given in
Table I. until k is fulfilled for the small time interval t_1 when
estimated as described below on this page.   Column 4 gives
the affinity constant calculated from p_0 and b_0 according to
equation (15).   Column 5 gives the time in minutes that
elapsed in each experiment before the first reading was taken ;
column 6 gives the free acid, p_t, present when the first read-
ing was taken, as determined analytically by the conductivity
at the moment   (see below).   Column 7 gives the free
base, b_t, present when the first reading was taken, as calcula-
ted from the concentrations of the free acid p_t and the salt
($1 - p_t$) according to equation (2) ; column 8 gives the total
substance, x_t, rearranged in time t_1.   It is equal to $p_t - b_t$. Col-
umn 9 gives the velocity constant as calculated for the small
time interval, t_1, from the preceding data ; it is found by
taking the concentration of the base for the short interval to
be equal to the mean of the concentration of the base when
t is 0 and when t is t_1 (column 5) ; then according to equation
(7) (p. 462).

$$\frac{x}{V t_1} = k \frac{b_0 + b_{t_1}}{2 V}$$

and $$k = \frac{2x}{t_1 (b_0 + b_{t_1})}. \tag{7'}$$

It is used as a test for the correctness of the values of columns
2, 3, and 4, which together with the observed values of col-
umns 5 and 6, determine k.   A small variation in the velocity
constant k has a very small effect on the value of the affinity

constant, K. Since the rearrangement is a monomolecular reaction whose velocity is dependent only on the concentration of the base, equation ($7'$) can be applied whether v is 32, 64, 128, or 256 liters, as in the terms in which x and b are expressed above, v is eliminated in equation ($7'$).

Table III.

v.	$100p_0$.	$100b_0$.	K.	t_1.	$100p_t$.	$100b_t$.	$100x$.	k.
32	18.0	18.0	810	2	18.9	16.94	1.96	0.056
32	18.0	18.0	810	2	18.9	16.94	1.96	0.056
64	24.70	24.7	790	$1\frac{1}{2}$	25.6	23.55	2.05	0.056
128	32.95	32.95	790	$1\frac{1}{2}$	34.1	31.3	2.80	0.058
128	30.65	30.65	[945]	$1\frac{1}{4}$	31.5	29.56	2.04	0.054
256	41.50	41.50	870	$1\frac{1}{4}$	42.55	39.74	2.81	0.055
256	41.30	41.30	880	$1\frac{1}{2}$	42.55	39.25	3.30	0.055

The mean of all the values of the affinity constant K, excepting (5) which was excluded on account of its obvious discrepancy, is K = 825. K = 800 is considered, however, the more correct, as the mean of the more reliable and concordant determinations 1 to 4, in less dilute solutions, where the rate of change is smaller, as the relative amount of free base is smaller and the observations, in consequence, more accurate.

Having determined the affinity constant of *o*-aminophenyl ethyl carbonate with reasonable accuracy, we will proceed to discuss the experimental method for following the course of rearrangement of the base in the aqueous solution of the hydrochloride and the method for calculating the velocity of rearrangement from the data obtained by observation.

The Velocity of the Rearrangement of o-Aminophenyl Ethyl Carbonate in the Aqueous Solution of the Hydrochloride, at 0°.

The experimental determination of the velocity of the rearrangement in a solution of the hydrochloride of *o*-aminophenyl ethyl carbonate is based on the following considerations: The two reactions expressed by the equations

$$RO_2CO.C_6H_4NH_3Cl + H_2O \; \rightleftharpoons$$

$$RO_2COC_6H_4NH_3OH + HCl, \quad (1)$$

$$RO_2COC_6H_4NH_3OH \;\rightarrow\; HOC_6H_4NHCO_2R + H_2O, \quad (4)$$
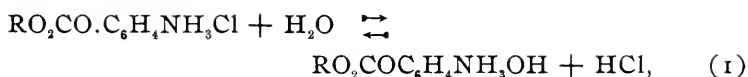
the one reversible and the second non-reversible, take place simultaneously in this solution. As the rearrangement proceeds according to (4) the amount of free base is diminished, and consequently to restore the disturbed condition of equilibrium of reaction (1) the reaction will proceed from left to right ; more free base is formed and acid thereby liberated, but, obviously, as the acid has increased, the amount of free base reproduced will be less than the amount rearranged ; and as every molecule of base reproduced by hydrolysis liberates a molecule of acid, the number of molecules of acid liberated in a given time will also be smaller than the number of molecules that have been rearranged. The increase in acid will, therefore, not be a direct measure of the number of molecules rearranged. Reaction (1) being ionic can be considered to proceed instantaneously to maintain a condition of equilibrium every moment.

The course of the reaction is marked, therefore, by a continuous increase in the amount of free hydrochloric acid and of the product of rearrangement, oxyphenylurethane, and by a continuous decrease in the amount of salt and free base present. The free base, being exceedingly weak and practically non-ionized in the presence of its hydrochloride, would have no effect on the conductivity of such a solution. The same is true for the oxyphenylurethane formed ; most of it is precipitated as it is formed and it is an exceedingly weak acid, and in the presence of free hydrochloric acid it is practically non-ionized and cannot affect the conductivity of the solution.[1] The conductivity depends, therefore, at any moment, solely on the relative concentrations of the salt and the free hydrochloric acid, and as the latter is a far better conductor the conductivity will steadily increase.

[1] Saturated solutions of *o*-oxyphenylurethane and of (3)-methyl-(6)-oxyphenylurethane gave, at 25°, specific conductivities of 0.00052. The conductivity of hydrochloric acid in solutions ranging from $N/32$ to $N/100$ was not changed by the addition of an excess of either urethane.

The hydrochloric acid and the salt have an ion, Cl′, in common, and as they have practically the same degree of ionization in equivalent dilute solutions, such solutions contain the common ion in the same concentration and may be considered to be isohydric. Now if we start with a $N/32$ solution of the hydrochloride of *o*-aminophenyl ethyl carbonate, and have, before any rearrangement has occurred, a condition of equilibrium as expressed in equation (1) with p per cent of 1 gram-molecule of free acid in 32 liters, and consequently $(1 - p)$ per cent of 1 gram-molecule of salt, we can consider the solution to consist of p cc. $N/32$ hydrochloric acid and $(1 - p)$ cc. $N/32$ salt solution—the acid and salt dividing the water between them in the proportion of $p : (1 - p)$.[1] The specific conductivities of the acid and salt considered separately will, therefore, be the specific conductivities for $N/32$ solutions and the observed specific conductivity of the solution will be :[2]

$$k_{32(obs)} = (1 - p)\, k_{salt(32)} + p k_{HCl(32)}. \tag{27}$$

Now as the rearrangement proceeds according to equation (4), we continue to have a $N/32$ solution of chlorine ions, and if p_t represents the per cent of 1 gram-molecule acid present, at any moment, $(1 - p_t)$ would still represent the per cent of salt present, (equation 1), and consequently equation (27) holds good throughout the whole course of the reaction. From (27) we find

$$p_t = \frac{k_{obs(32)} - k_{salt(32)}}{k_{HCl(32)} - k_{salt(32)}}. \tag{28}$$

In this equation the observed specific conductivity $k_{obs(32)}$ is determined by conductivity measurements with the Kohlrausch apparatus ; the specific conductivity of the non-hydrolyzed salt $k_{salt(32)}$ was determined as shown above and found to be 0.001369 at 0°. The specific conductivity of $N/32$ hydrochloric acid, $k_{HCl(32)}$, at 0° was found by Jones to be 0.007300. We are thus able to determine for any moment the

[1] Arrhenius : Ztschr. phys. Chem., **2**, 17 (1888); **31**, 206 (1899). See also the preceding paper in this JOURNAL by Stieglitz and Derby.
[2] Stieglitz and Derby : *loc. cit.*

amount of free hydrochloric acid, p_t, present in the solution during the course of the rearrangement by means of a conductivity determination at the required time.

The concentration of the base, b_t, at any moment can be determined from that of the acid. For when the concentration of the acid is p_t per cent of 1 gram-molecule in 32 liters, the concentration of the salt, s_t, is $(1 - p_t)$ per cent, and the concentration of the base, b_t, is then determined for any moment from equation (2):

$$C_s = KC_bC_a,$$

or

$$\frac{1 - p_t}{V} = K\frac{b_t}{V} \cdot \frac{p_t}{V}, \tag{29}$$

and

$$b_t = \frac{V}{K} \times \frac{1 - p_t}{p_t}. \tag{29'}$$

K is the affinity constant of the free base and was found to be 800 (Table III., p. 475). For the concentration of the base, b_t, at any moment we have, then,

$$b_t = \frac{32}{800} \times \frac{1 - p_t}{p_t}. \tag{29''}$$

For the amount of substance, x_t, rearranged in time, t, we have,

$$x_t = 1 - (s'_t + b_t)$$
$$= p_t - b_t.$$

From the values thus determined we can ascertain if all the aminophenyl ethyl carbonate, whether present as salt or base, is rearranging with equal velocity, by calculating the value of the velocity constant k_τ according to equation (6'):

$$k_\tau = \frac{1}{t} \log. \text{ nat. } \frac{C}{C - x}$$

$$= \frac{1}{t} \log. \text{ nat. } \frac{1}{1 - x^t}. \tag{6'}$$

It is shown (see Table IV., column 8, in which common logarithms were used for this constant) that no constant value for k_T is found—consequently, the free base and salt molecules do not rearrange indifferently.

By calculating the value of the velocity constant k_B according to equation (12), we can ascertain whether only the molecules of the free base are undergoing rearrangement. Equation (12) becomes

$$k_B.t = -\frac{K_1}{1 + K_1 b_t} + K_1 \log. \text{nat.} \left(K_1 + \frac{1}{b_t}\right) - \log. \text{nat.} \ b_t$$

$$+ \left[\frac{K_1}{1 + K_1 b_0} - K_1 \log. \text{nat.} \left(K_1 + b_0\right) + \log. \text{nat.} \ b_0\right].$$

$$K_1 = \frac{K}{V} \text{ or } \frac{800}{32} = 25.$$

b_0, the concentration of the base when t is 0, has the value 0.1810 molecule in 32 liters (see Table III.). Introducing these values we obtain:

$$k_B.t = -\frac{1}{0.040 + b_t} + 25 \log. \text{nat.} \left(25 + \frac{1}{b_t}\right) -$$
$$\log. \text{nat.} \ b_t - 82.664. \quad (30)$$

As is seen from the following table, where the values of k_B are given in column 7, they show a very good agreement for the long time interval between $t = 20$ and $t = 600$, when it was possible to make the conductivity readings with considerable accuracy. During the first twenty minutes when the amount of the free base was large and the conductivity changing, therefore, very rapidly, parallel with the rapid change of the base, the readings with the Kohlrausch apparatus and a telephone were necessarily much less accurate ; the constant was determined, therefore, only for the time after $t = 20$. The determination leaves no doubt whatever, first, that the substance undergoing rearrangement in the solution of the hydrochloride of o-aminophenyl ethyl carbonate is the free base formed by hydrolysis, and that its rearrangement is a

monomolecular reaction, the velocity for which at a given temperature is dependent only on the concentration of the base, and second, that the rearrangement is influenced by the presence of the hydrochloric acid only in so far as the latter converts the free base into the salt.

The value for the velocity constant, k_B, can also be calculated from the experimental data by the following very close approximation: for small time intervals (*e. g.*, $t = 10$ minutes) the concentration of the base may be considered to be the average of its concentrations at the beginning and the end of the time interval. If b_0 represents the concentration of the base when $t = 0$, and b_1, b_2, $\ldots\ldots\ldots b_{n-1}$, b_n express the concentrations at the end of the first, second, $(n-1)$th and nth time interval at ten minutes, then for a monomolecular reaction dependent on the concentration of the base,

$$k = \frac{x}{10\left(\dfrac{b_0}{2} + b_1 + \cdots \cdots b_{n-1} + \dfrac{b_n}{2}\right)}. \qquad (30')$$

The results for the velocity constant calculated on the basis of this formula are given in column 6 as k'_B; for the time beyond $t = 150$, interpolated values were used and a member, b, included in the summation for every ten minute interval. The results agree very well with those obtained by means of the more rigorous formula (30).

The table follows : Column 1 gives the time in minutes ; 2, the observed specific conductivities ; 3, the concentration of acid, p_t, in percentages of 1 molecule as calculated according to (28) ; 4 gives the percentage of free base, b_t, present as calculated from (29″) ; in column 5 the percentage of rearranged substance is given ; 6 gives the velocity constant calculated according to (30′) ; 7 the same calculated according to (30). The last column gives the results of the calculation of a velocity constant on the basis of the ordinary equation for a monomolecular reaction involving all of the substance present (equation (6′)).

Table IV.

t.	$10^6\,k_{obs}$.	$100p_t$.	$100b_t$.	$100x$.	k'_B.	k_B.	k_T.
0		18.1	18.10				
2	2489	18.9	17.14	1.76			
10	2643	21.5	14.61	6.89	[0.042]	[0.0425]	311
20	2872	25.3	11.81	13.49	[0.046]	[0.0464]	315
30	3181	30.55	9.10	21.45	[0.0535]	0.0566	349
40	3369	33.7	7.87	25.83	[0.0535]	0.0555	324
50	3640	38.2	6.47	31.73	0.0570	0.0610	331
60	3800	40.9	5.78	35.12	0.0570	0.0600	314
70	3904	42.7	5.37	37.33	0.0556	0.0571	291
80	4070	45.5	4.79	40.69	0.0563	0.0583	284
90	4190	47.5	4.42	43.08	0.0560	0.0570	272
100	4337	50.0	4.00	46.00	0.0567	0.0586	268
110	4404	51.2	3.81	47.39	0.0558	0.0567	254
120	4520	53.1	3.53	49.57	0.0560	0.0569	248
130	4642	55.2	3.25	51.95	0.0565	0.0578	245
140	4720	56.5	3.08	53.42	0.0561	0.0571	237
150	4825	58.3	2.85	55.50	0.0560	0.0581	234
180	5052	62.1	2.44	59.70	0.0562	0.0571	219
210	5301	66.3	2.03	64.30	0.0569	0.0588	213
240	5401	68.0	1.88	66.10	0.0556	0.0554	196
270	5651	72.2	1.54	70.60	0.0568	0.0591	197
300	5725	73.6	1.435	72.40	0.0562	0.0574	186
330	5881	76.1	1.256	74.80	0.0563	0.0572	181
360	6048	79.0	1.063	78.00	0.0572	0.0601	183
390	6134	80.4	0.975	79.40	0.0569	0.0592	176
420	6180	81.2	0.926	80.30	0.0565	0.0571	168
540	6410	85.1	0.700	84.40	0.0556	0.0567	149
650	6610	88.4	0.525	87.90	0.0564	0.0581	153
1500	7301	100.0	0.000	100.0			
				Means,	0.0564	0.0578	

k_B can also be calculated as follows. Equation (12) gives:

$$k(t_2 - t_1) = -\frac{K_1}{1 + K_1 b_2} + \frac{K_1}{1 + K_1 b_1} +$$
$$K_1 \log. \text{ nat. } \frac{K_1 + \dfrac{1}{b_2}}{K_1 + \dfrac{1}{b_1}} + \log. \text{ nat. } \frac{b_1}{b_2}. \quad (31)$$

A few estimations for time intervals chosen at random follow :

Table V.

t_2.	t_1.	$t_2 - t_1$.		k_B.
100	60	40		0.0564
150	50	100		0.0566
150	80	70		0.0578
300	100	200		0.0555
600	100	500		0.0580
			Mean,	0.0569

In a duplicate determination of the velocity of rearrangement, readings were not made as often as above. The agreement between the two series is satisfactory, as shown by the following table :

Table VI.

t.	$10^6 \times k_{obs}$.	$100 p_t$.	$100 b_t$.	$100 x$. I.	$100 x$. II.	k_B.
0		18.10	18.10			
2	2489	18.90	17.20	1.7	1.7	
30	3169	30.35	9.18	21.4	21.2	0.0556
62	3816	41.25	5.70	35.60	35.55	0.0593
77	3975	43.93	5.10	39.55	38.80	0.0557
167	4949	60.35	2.63	57.90	57.70	0.0569
390	6112	80.00	1.00	79.40	79.00	0.0581
					Mean,	0.0571

In the fifth column, under $100x$, the total rearrangement for equal times, is compared for the duplicates.

Orthoaminophenyl Methyl Carbonate.

The determinations of the affinity constant of o-aminophenyl methyl carbonate and of the velocity constant of its rearrangement in the aqueous solution of its hydrochloride were carried out in the same way as in the case of the ethyl ether, as just described. By putting the molecular conductivities μ_v of the non-hydrolyzed chloride equal to the corresponding conductivities of the non-hydrolyzed hydrochloride of the isomeric base, p-aminophenyl methyl carbonate, as determined above (p. 470), it was possible to determine the affinity constant according to Walker's and Bredig's method.

As there was some rearrangement of the hydrochloride with production of an excess of acid during the short time interval between the solution of the salt and the first readings, the values obtained by using these first readings for an approximate determination of the affinity constants were corrected with the aid of a preliminary approximate determination of the value of the velocity constant of rearrangement—in exactly the same way as described above in detail for the ethyl ether. It will only be necessary to give the experimental data in the following tables. The first shows the approximate estimation of the affinity constant K :

Table VII.

v.	M_v.		μ_v.	$100x$.		K.	
	I.	II.		I.	II.	I.	II.
32	78.5	....	45.90	17.37	....	877	...
64	94.78	93.5	47.25	25.08	24.20	761	829
128	108.16	108.16	48.60	31.30	31.30	899	899
256	125.61	125.60	49.50	39.97	39.97	960	960
					Mean,	K =	880

The approximate velocity constant of rearrangement, k, determined as on page 473, was found to be 0.090 as the mean of eighteen observations (from twenty-three to two hundred and twenty-nine minutes) ; the values ranged from 0.0875 to 0.0924, but fourteen were between 0.089 and 0.0915. The correction of the data of the previous table, with the help of this approximate velocity constant ($k = $ 0.090) is given in the next table. The method of correction and the meaning of the columns are explained in connection with Table III. :

Table VIII.

v.	$100p_0$.	$100b_0$.	K.	t_1.	$100p_{t_1}$.	$100b_{t_1}$.	$100x$.	k.
32	16.10	16.10	1035	2	17.37	14.70	2.67	0.087
64	22.40	22.40	990	2	24.20	20.25	3.95	0.092
64	23.30	23.30	[905]	2	25.08	21.13	3.95	0.089
128	29.40	29.40	1045	$1\frac{3}{4}$	31.30	26.90	4.40	0.089
128	29.40	29.40	1045	$1\frac{3}{4}$	31.30	26.90	4.40	0.089
256	38.40	38.40	1070	$1\frac{1}{4}$	40.00	35.89	4.11	0.089
256	38.40	38.40	1070	$1\frac{1}{4}$	40.00	35.89	4.11	0.089
			Mean (excluding the third) K =				1040	

The following Table IX., gives the final data for the calculation of the velocity constant, k_{B}, and the results obtained.

The nature of the data of the first five columns is the same as explained above for Table IV. In column 7 appear the values of the velocity constant as calculated from the concentrations of the base, b_t, for the various time intervals, t, according to equation (12). As K_1 is K : V or 1040 : 32 (*i. e.*, 32.5), and the initial concentration of the base, b_0, is 0.1607 molecule, the equation reads for this case :

$$k_{\text{B}}t = -\frac{1}{0.03077 + b_t} + 32.5 \text{ log. nat. } \left(32.5 + \frac{1}{b_t}\right) - $$
$$\text{log. nat. } b_t - 115.458.$$

In column 6 the velocity constant (k'_{B}) is given as calculated by a formula corresponding to that given in equation (30′) that can very readily be adapted to the varying time intervals used.

The table shows both by the rigorous method of calculation (k_{B}) and the less rigorous method (k'_{B}) that the reaction of rearrangement is undoubtedly a monomolecular one, dependent wholly on the concentration of the free base formed by hydrolysis. While the values vary somewhat more than in the previous case, there is no question that for over eight hours a constant rate of change of the base is shown ; at that time 90 per cent of the substance had been rearranged. It is also clear that the velocity of rearrangement is nearly twice as great as for the ethyl ether of the same series $(k = 0.0578)$, a fact which accounts perhaps for the somewhat greater range of experimental error in the observations :

Table IX.

Time.	$10^6 \times k_{obs.}$	$100p_t.$	$100b_t.$	$100x.$	$k'_B.$	$k_B.$
0		16.07	16.07			
2	2454	17.40	14.60	2.80		
20	3094	28.30	7.80	20.50		[0.0959]
29	3401	33.55	6.10	27.45	[0.0968]	0.0981
39	3694	38.53	4.91	33.62	0.0993	0.1028
49	3904	42.10	4.23	37.87	0.0984	0.1018
59	4138	46.10	3.60	42.50	0.1004	0.1042
69	4348	49.68	3.12	46.56	0.1019	0.1064
89	4642	54.70	2.548	52.15	0.1015	0.1049
109	4880	58.77	2.159	56.61	0.1010	0.1032
129	5112	62.72	1.829	60.89	0.1014	0.1031
149	5286	65.68	1.608	64.07	0.1008	0.1029
169	5482	68.50	1.415	67.08	0.1009	0.1023
189	5613	71.24	1.247	69.99	0.1010	0.1026
209	5803	74.50	1.053	73.43	0.1027	0.1074
229	5881	75.81	0.982	74.83	0.1018	0.1041
270	6027	78.30	0.853	77.45	0.1002	0.0979
330	6246	82.04	0.674	81.37	0.0994	0.0966
390	6482	86.06	0.498	85.56	0.1102	0.1002
450	6556	87.35	0.445	86.90	0.0986	0.0932
510	6736	90.40	0.326	90.07	0.0995	0.0990
(1440)	7280	100.00		100.00		
				Mean,	0.1005	0.1017

Cresol Derivatives.

4-Methyl-2-aminophenyl Ethyl Carbonate,

$C_2H_5O.\overset{(1)}{C}O.C_6H_3\overset{(4)}{(CH_3)}\overset{(2)}{N}H_2$.—As just shown, the substitution of an ethyl for a methyl group in the carbalkoxyl chain of *o*-aminophenyl alkyl carbonates reduces the velocity constant of rearrangement by nearly 50 per cent. A study was also made of the influence of the substitution of a methyl group in the benzene nucleus in place of hydrogen and the influence of the position occupied by the methyl group.

For this purpose the velocity constants of rearrangement of three *o*-aminocresyl ethyl carbonates were determined, compared with each other and those of the phenyl derivatives.

The conclusions arrived at will appear below, after the experimental material has been given.

For these determinations, by the methods described above, it was above all essential to know the molecular conductivities of the non-hydrolyzed salts. Advantage was taken of the fact that one of the isomers, 4-methyl-2-aminophenyl ethyl carbonate, the derivative of paracresol, rearranges so slowly that molecular conductivities of its hydrochloride could be determined with sufficient accuracy by the method developed for the stable hydrochlorides of the p-aminophenyl alkyl carbonates.

If p_{32} and p_{128} represent the degree of hydrolysis of the hydrochloride of 4-methyl-2-aminophenyl ethyl carbonate in $N/32$ and $N/128$ normal concentrations, we find with the aid of relations as expressed in equations (14) to (22), inclusive, by the methods described in detail above that

$$p_{32} = 0.546 \, p_{128}.^{[1]} \tag{32}$$

Combining (14) and (32) we have now exactly

$$\frac{M_{32} - \mu_{32}}{\mu_{HCl(32)} - \mu_{32}} = 0.546 \, \frac{M_{128} - \mu_{128}}{\mu_{HCl(128)} - \mu_{128}}. \tag{33}$$

M_{32}, as found, was 73.47 in reciprocal mercury units and M_{128} 102.70. $\mu_{32(HCl)}$ is 233.6, $\mu_{128(HCl)}$ is 239.0. $\Delta 128.32$ is 2.7.

Inserting these values in (33) and solving for μ_{32}, we find μ_{32} is 42.6. This value, it may be added, is also in perfect agreement with the change in molecular conductivity which was to be expected from the introduction of a methyl group into the hydrochloride of aminophenyl ethyl carbonate, for which we found $\mu_{32} = 43.8$.

[1] A second correction of this relation is also in this case unnecessary, since when we use the final values for p_{32} and p_{128} as determined below, we find $p_{32} = 0.546 \, p_{128}$, which is identical with (32).

From μ_{32}, the molecular conductivities for 1–32, 1–128, and 1–256 normal solutions of the salt were derived as on page 469.

The following table gives the data for the determination of the affinity constant, K, for 4-methyl-2-aminophenyl ethyl carbonate :

Table X.

v.	M_v.		μ_v.	$100x$.		K.	
	I.	II.		I.	II.	I.	II.
32	73.47	73.47	42.60	16.16	16.16	1027	1027
64	87.23	86.50	43.95	22.47	22.07	985	1025
128	102.72	101.82	45.30	29.63	29.18	1026	1065
256	122.24	122.24	46.20	39.25	39.25	1010	1010

<div align="right">Mean, K = 1022</div>

The agreement in the values of K found is very satisfactory, and the results confirm the reliability of the method used for the determination of the molecular conductivities.

The velocity of the rearrangement of 4-methyl-1-aminophenyl ethyl carbonate at 0° was then determined in N/32 solution of the hydrochloride by observations of the specific conductivity of the solution at frequent intervals (column 1 of Table XI.). From the specific conductivity (column 2), the amount of free acid (column 3) present at any moment was ascertained according to equation (28).

The specific conductivity (k_{32}) of the non-hydrolyzed salt in N/32 dilution at 0° is (μ_{32} : 32000) or 0.001331 in mercury units. The specific conductivity of N/32 hydrochloric acid at 0° is 0.007300. Inserting these values in (28) we have :

$$p_t = \frac{k_{obs} - 0.001331}{0.007300 - 0.001331}.$$

The concentration of the free base, b_t, at any moment (column 4) follows from the concentrations of the free acid, p_t, and the salt $(1 - p_t)$ according to equation (29') ; as V is 32 and the affinity constant, K, is 1020, we have :

$$b_t = \frac{32}{1020} \cdot \frac{1 - p_t}{p_t}.$$

For the amount of rearranged substance, x_t (column 5) for any time interval we have :

$$x_t = p_t - b_t.$$

The velocity constant, k_B, (column 7) of the rearrangement was calculated according to a modified form of equation (31), *viz* :

$$k(t_2 - t_1) = - \frac{K_1}{1 + K_1 b_{t_2}} + K_1 \log. \text{nat.} \left(K_1 + \frac{1}{b_{t_2}} \right) - \log. \text{nat} \, b_{t_2}$$

$$+ \left[\frac{K_1}{1 + K_1 b_{t_1}} - K_1 \log. \text{nat.} \left(K_1 + \frac{1}{b_{t_1}} \right) + \log. \text{nat.} \, b_t \right].$$

Putting $t_1 = 12$, b_{t_1} is found to be 0.1578.

$$K_1 = \frac{K}{V} \text{ or } \frac{1020}{32} = 31.875$$

and
$$\frac{1}{K_1} = 0.03137.$$

Introducing these values and the calculated value of the bracketted constant expression in the above integration, we have :

$$k(t - 12) = - \frac{1}{0.03137 + b_t} +$$

$$31.875 \log. \text{nat.} \left(31.875 + \frac{1}{b_t} \right) - \log. \text{nat.} \, b_t - 112.707.$$

Column 6 gives the velocity constant, k'_B, calculated from a formula of summation corresponding to equation (30'), and adapted to the time intervals used.[1]

The tabulated results follow :

[1] Three to five minutes' intervals were used until $t = 88$. Only the observations made in the main intervals are tabulated, in the interest of economy of space ; the intermediate readings for the shorter time intervals were used, however, in estimating k'_B.

Table XI.

$t.$	$10^6 \times k_{obs.}$	$100pt.$	$100bt.$	$100x.$	$k'_{\mathrm{B}.}$	$k_{\mathrm{B}.}$
2	2296	16.17	16.17			
6	2296	16.17	16.17			
12	2321	16.58	15.78	0.80		
21	2419	18.23	14.07	4.16	[0.0250]	[0.0252]
31	2489	19.40	13.03	6.37	0.0208	0.0204
41	2564	20.65	12.05	8.60	0.0198	0.0196
53	2642	21.96	11.15	10.81	0.0187	0.0185
63	2726	23.37	10.29	13.08	0.0192	0.0190
73	2816	24.88	9.47	15.41	0.0198	0.0198
83	2862	25.65	9.09	16.56	0.0189	0.0188
88	2901	26.30	8.79	17.51	0.0190	0.0190
98	2961	27.30	8.35	18.95	0.0188	0.0188
108	3045	28.71	7.79	20.92	0.0193	0.0193
118	3100	29.64	7.45	22.19	0.0191	0.0190
128	3157	30.59	7.12	23.47	0.0190	0.0189
138	3216	31.59	6.79	24.80	0.0190	0.0188
148	3277	32.60	6.49	26.11	0.0189	0.0190
158	3341	33.68	6.18	27.50	0.0192	0.0192
168	3368	34.12	6.05	28.07	0.0188	0.0187
178	3435	35.25	5.76	29.49	0.0190	0.0190
198	3505	36.43	5.47	30.96	0.0186	0.0183
218	3578	37.64	5.20	32.44	0.0183	0.0178
238	3654	38.03	4.92	34.01	0.0181	0.0177
278	3817	41.66	4.39	37.27	0.0181	0.0176
318	3994	44.62	3.894	40.73	0.0183	0.0181
358	4128	46.86	3.557	43.30	0.0182	0.0180
398	4230	48.58	3.322	45.26	0.0180	0.0176
438	4381	51.10	3.002	48.10	0.0182	0.0180
498	4496	53.02	2.780	50.24	0.0179	0.0173
536	4592	54.62	2.606	52.01	0.0179	0.0174
4800	7250	100.00		100.00		
				Mean,	0.0188	0.0186

It is apparent that the rearrangement is again a monomolecular reaction dependent on the concentration of the free base and proceeding with a practically constant velocity for the nine hours that the determination included ; the results therefore, confirm those obtained in the phenyl series. It is noteworthy, too, that the methyl group introduced into the ben-

zene ring in the para position, as regards the migrating carb-ethoxyl group, should reduce the velocity of rearrangement to about one-third the value of the rearrangement constant of *o*-aminophenyl ethyl carbonate, but it has not very materially affected the relative affinity constants of the bases (1020 and 800, respectively).

5-Methyl-2-aminophenyl Ethyl Carbonate,

$C_2H_5O_2CO.C_6H_3(CH_3)NH_2$.—In an aqueous solution of the hydrochloride of 5-methyl-2-aminophenyl ethyl carbonate, the free base rearranges so rapidly, again, that in estimating the affinity constant of the base from the observation of molecular conductivities, a correction must be made for the change in the solutions in the one to two minutes that elapsed before the first conductivity reading could be taken. The method used is the same as that given in tables I.–III., and it will be sufficient to give the results in tabulated form :

Table XII.— The Approximate Affinity Constant.

v.	M_v.	$\mu_v.^1$	$100x$.	K.
32	69.05	42.60	13.85	1438
64	77.37	43.95	17.33	1760
128	92.74	45.30	24.50	1612
			Mean,	K = 1600

The velocity of rearrangement, k, as calculated on the basis of this approximate value of the affinity constant, was found to be 0.067. The correction of the data of the previous table for the time, t, that elapsed before M_v was observed, follows :

Table XIII.[2]

v.	$100 \times p_0$.	$100 \times b_0$.	K.	t_1.	$100 \times p_t$.	$100 \times b_t$.	$100x$.	k.
32	13.05	13.05	1630	2	13.85	12.18	1.67	0.066
64	16.35	16.35	2000	2	17.33	15.24	2.09	0.066
128	23.35	23.35	1800	$1\frac{3}{4}$	24.50	21.92	2.58	0.065
	Mean, K = 1800							

[1] These values for the molecular conductivities were put equal to those determined above for the isomer.

[2] See Table III. for the meaning of the columns.

For the determination of the rearrangement velocity of 5-methyl-2-aminophenyl ethyl carbonate the integral equation (12) may be applied with the following values of the known constants :

$$K_1 = \frac{K}{V} \text{ or } \frac{1800}{32} = 56.25 ;$$

$$\frac{1}{K_1} = 0.01778.$$

b_0, the concentration of the base when t is o, is 0.1247.

Inserting these values in equation (12) and calculating the result for the constant bracketted expression, we obtain :

$$k_B t = -\frac{1}{0.01778 + b_t} +$$

$$56.25 \text{ log. nat. } \left(56.25 + \frac{1}{b_t}\right) - \text{log. nat. } b_t - 229.277.$$

Equation (28) gives the concentration of the free acid, p_t, after insertion of the known and found values :

$$p_t = \frac{k_{obs} - 0.001331}{0.007300 - 0.001331}.$$

Equation (29') gives the concentration of the free base, b_t :

$$b_t = \frac{32}{1800} \times \frac{1 - p_t}{p_t}.$$

The amount of rearranged substance, x, is :

$$x_t = p_t - p_t.$$

Table XIV. gives the tabulated results :

Table XIV.

$t.$	$10^6 \times k_{obs}.$	$100 \times p_t.$	$100 \times b_t.$	$100x.$	$K_B.$
0		12.47	12.47		
2	2158	13.85	11.06	2.79	
10	2353	17.12	8.61	8.51	
22	2642	21.97	6.31	15.66	
32	2788	24.45	5.49	18.96	0.074
42	2992	27.83	4.61	23.22	0.076
52	3123	30.04	4.14	25.90	0.074
62	3271	32.50	3.69	28.81	0.074
72	3401	34.68	3.35	31.33	0.074
82	3541	37.03	3.02	34.01	0.075
92	3623	38.40	2.85	35.55	0.072
102	3694	39.59	2.71	36.88	0.070
112	3816	41.64	2.49	39.15	0.072
122	3903	43.08	2.35	40.73	0.071
132	3994	44.62	2.21	42.41	0.071
142	4089	46.21	2.07	44.14	0.072
172	4294	49.63	1.81	47.82	0.070
197	4404	51.47	1.68	49.79	0.067
237	4771	57.62	1.31	56.31	0.074
287	4978	61.10	1.13	59.97	0.072
327	5096	63.09	1.04	62.05	0.069
372	5300	66.50	0.90	65.60	0.070
427	5452	69.05	0.80	68.25	0.069
482	5631	72.05	0.69	71.36	0.070
657	6026	78.67	0.48	77.19	0.069
2880	7277	100.00	0.00	100.00	....

Mean,   0.0717

Again we find that the rearrangement proceeds with a constant velocity, when the rate of change is referred to the concentration of the free base present in the solution. The shifting of the methyl group from the para to the meta position of the benzene ring (referred to the migrating carbethoxyl group) has increased the velocity of rearrangement nearly four-fold (0.0717 as compared with 0.0186), and has made the velocity constant of the reaction even surpass that of the non-methylated lower homologue of the phenyl series (0.0717 as compared with 0.0578 of the *o*-aminophenyl ethyl carbonate).

6-Methyl-2-aminophenyl Ethyl Carbonate,

$C_2H_5O_2\overset{(1)}{C}O\overset{(6)}{C_6H_3}\overset{(2)}{C}H_3NH_2.$—6-Methyl-2-aminophenyl ethyl carbonate is the last base for which the affinity constant and the

velocity of rearrangement were determined quantitatively by the methods used in this investigation. The rate of rearrangement is again so great that in determining the affinity constant from the observed molecular conductivities a correction was made in the usual way for the time elapsed before the readings could be taken (one to two minutes). The tabulated results follow :

Table XV. — The Approximate Affinity Constant,

$v.$	$M_v.$		$\mu_v.$[1]	$100x.$		K.	
	I.	II.		I.	II.	I.	II.
32	78.50	77.40	42.60	18.80	18.22	735	790
64	99.72	94.59	43.95	26.33	26.26	680	685
128	108.82	108.82	45.30	32.79	32.79	800	800
256	125.62	125.20	46.20	41.00	40.77	900	910

Mean, K $=$ 790

The approximate velocity constant, k, of rearrangement was found in the usual way to be 0.067. The corrected data of the previous table follow, showing the corrected affinity constant of 6-methyl-2-aminophenyl ethyl carbonate[2] :

Table XVI.

$v.$	$100p_0.$	$100b_0.$	K.	$t.$	$100pt.$	$100bt.$	$100x.$	$k.$
32	17.75	17.75	835	2	18.80	16.54	2.26	0.066
32	17.30	17.30	880	2	18.22	16.24	1.98	0.067
64	24.90	24.90	775	2	26.23	23.10	3.23	0.067
64	24.85	34.85	780	2	26.26	23.10	3.16	0.066
128	31.30	31.30	900	$1\frac{3}{4}$	32.79	29.23	3.56	0.067
128	31.30	31.30	900	$1\frac{3}{4}$	32.79	29.23	3.56	0.067
256	39.78	39.78	975	$1\frac{1}{4}$	41.00	37.87	3.17	0.065
256	39.50	39.50	990	$1\frac{1}{4}$	40.77	37.45	3.32	0.069

Mean, K $=$ 880

The velocity constant of rearrangement of this base was determined by the same method as in the previous cases. The known constants in equation (12) have the following values :

$$K_1 = \frac{K}{V} \text{ or } \frac{880}{32} = 27.5;$$

$$\frac{1}{K_1} = 0.03636.$$

b_0, the concentration of the base when t is 0, is 0.1734. Substituting these values in (12) we have :

[1] See table X.

[2] See Table III. for the method of correction and the meaning of the columns.

$$kt = -\frac{1}{0.03636 + b_t} +$$

$$27.5 \log. \text{ nat. } (27.5 + b_t) - \log. \text{ nat. } b_t - 93.379.$$

The concentration of the acid, p_t, at any moment is determined by the observed specific conductivities according to (28):

$$p_t = \frac{k_{obs} - 0.001331}{0.007300 - 0.001331}.$$

The concentration of the free base, b_t, is found according to (29'):

$$b_t = \frac{32}{880} \times \frac{1 - p_t}{p_t}.$$

The amount of rearranged substance, x_t, is:

$$x_t = p_t - b_t.$$

Table XVII.

t.	$10^6 k_{obs}$.	$100 \times p_t$.	$100 \times b_t$.	$100x$.	k_B.
0		17.34	17.34		
2	2454	18.81	15.69		
11	2726	23.37	11.92		
20	2987	27.75	9.47	18.28	[0.072]
30	3210	31.48	7.91	23.57	0.069
40	3435	35.25	6.68	28.57	0.069
51	3654	38.93	5.70	33.23	0.069
61	3817	41.66	5.09	36.57	0.068
71	3994	44.62	4.51	40.11	0.069
81	4138	47.03	4.10	42.93	0.068
91	4241	48.76	3.82	44.94	0.066
101	4381	51.10	3.48	47.62	0.067
111	4496	53.03	3.22	49.81	0.067
121	4616	55.04	2.97	52.07	0.067
131	4718	56.74	2.77	53.97	0.067
141	4797	58.24	2.61	55.63	0.067
151	4879	59.40	2.49	56.92	0.066
161	4993	61.34	2.39	59.05	0.067
184	5127	63.59	2.08	61.51	0.065
218	5367	67.60	1.74	65.86	0.065
237	5452	69.05	1.63	67.42	0.064
317	5822	75.24	1.20	74.05	0.063
382	6026	78.68	0.98	77.70	0.061
449	6245	82.34	0.78	81.56	0.062
509	6432	85.45	0.62	84.83	0.064
517	6762	91.00	0.36	90.64	0.061
1440	7216	100.00		100.00	

Mean, K = 0.066

The values for the velocity constant, k, show a satisfactory agreement, particularly for the first four hours, when the rate of change and the concentration are most favorable for accurate determinations. The slight falling off, which is noticeable in this and in most of the other determinations, is possibly due to the fact that the oxyphenylurethane which is precipitated may carry with it small amounts of the free base and gradually weaken the solution somewhat.

Summary of Part I.

The seven aminophenyl alkyl carbonates which were examined quantitatively show the following affinity constants, K_{aff}, and velocity constants of rearrangement, k:

Table XVIII.

		$K.^{1}$	$10^{14} \times K_{aff}.$	$k.$
I.	4 aminophenyl methyl carbonate	23200	27800	
II.	4 " ethyl "	22050	26500	
III.	2 " methyl "	1040	1250	0.1017
IV.	2 " ethyl "	800	960	0.0578
V.	4 methyl-2-aminophenyl ethyl carbonate	1020	1225	0.0186
VI.	5 methyl-2-aminophenyl ethyl carbonate	1800	2160	0.0717
VII.	6 methyl-2-aminophenyl ethyl carbonate	880	1050	0.0659

A consideration of the table leads to the following conclusions:

1. Whereas the p-aminophenyl alkyl carbonates have affinity constants of the order of that of aniline ($K = 41000$),[2] the ortho derivatives are, without exception, very much weaker bases and their affinity constants are only about one thousand times as large as the dissociation constant of water.[3] This is what was expected from the greater proximity of the negative carbonate group, (OCO_2R), to the basic group, and the result is

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[1] K signifies that the affinity constant of the base is K times greater than the degree of dissociation of water, 1.2×10^{-14}. See page 460. $K_{aff} = K \times 1.2 \times 10^{-14}$.

[2] Bredig: *Loc. cit.*

[3] The affinity constant of water, $[K_{H_2O} \times C_{H_2O} = C_H \times C_{OH}]$, is $1 : 55.5$ of its dissociation constant, $[C_H \times C_{OH}]$, as there are 55.5 gram-molecules of water in 1 liter. The bases have therefore affinity constants, which are only about 55,000 times as great as that of water.

in accord with the observations of Ostwald and others on the relative influence of negative groups in the ortho and para positions on the affinity constants of acids.

Of the three cresyl derivatives the base which has the methyl group in para position to the amino group (5-methyl-2-aminophenyl ethyl carbonate) was found to be decidedly stronger than the isomeric bases, in which methyl is in the meta position to the amino group. This is in agreement with Bredig's determinations of the affinity constants of the toluidines—*p*-toluidine is more than twice as strong a base as *m*-toluidine.

2. The velocity constants obtained from five independent series of determinations for the bases named, in experiments covering from ten to twelve hours each, and continued until the rearrangement into oxyphenylurethanes was practically completed,[1] fully justify the main conclusion that in the salt solutions the rearrangement depends wholly on the presence of the free base in the solution, that the free acid retards the rearrangement by salt formation, and that the actual rate of rearrangement is the result of two simultaneous reactions, one a non-reversible reaction of rearrangement of the free base, the other, a reversible reaction, which results in a condition of equilibrium between the salt, water, the free acid, and the free base.

3. The actual velocity constants are of a rather high order, inasmuch as a nearly complete rearrangement (90 per cent) would occur at 0° in from forty (2-aminophenyl methyl carbonate) to one hundred and thirty minutes (4-methyl-2-aminophenyl ethyl carbonate), if all the base could be kept free continuously in such a solution.[2] This unquestionable result is rather surprising, because Ransom and the one of us were able to isolate and examine free *o*-aminophenyl ethyl

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[1] In the case of 4-methyl-2-aminophenyl ethyl carbonate, which rearranges very slowly, only 52 per cent was rearranged at the end of nine hours, when the quantitative measurements were interrupted by the fall of night. In all cases the measurements were continued the next morning, the vessel remaining in ice over night, but no attempt was made to use the results for quantitative calculations, owing to the long break in the observations.

[2] For such a hypothetical case $t = \frac{1}{k} \log \cdot \frac{C}{C - x}$.

carbonate, and while it rearranged spontaneously, even in the absence of water, the change was far from complete even in an hour at ordinary temperature. Moreover, we have been able to show that in an anhydrous, alcohol-free, ethereal solution of *o*-aminophenyl ethyl carbonate, there is still some base present after two and one-half days. It cannot be decided at present whether this characteristic feature of the rearrangement of the base is due simply to the formation of an acid, though a weak acid substance, oxyphenylurethane, which, in an ethereal solution of the free base or dissolved in the oily base itself, may retard its rearrangement somewhat as hydrochloric acid does in an aqueous solution, or whether there is a direct influence of the solvent as such on the velocity constant. It surely cannot be due, however, to any catalytic action of the hydrochloric acid in the aqueous solution of the hydrochloride, as one might suspect, as such an action would result in a rapid increase in the value of the velocity constant, *k*, which, as the experimental data show, does not occur.

4. The more or less positive character of the amino group as measured by the affinity constants, K, does not seem to have any paramount influence in determining the tendency of the base to undergo rearrangement as measured by the rate of rearrangement. That is shown clearly by comparing VI with VII, V with VI or VII, and particularly III with V in Table XVIII. With practically identical affinity constants, the last two bases show velocity constants standing in the ratio 5 : 1. The velocity constant depends more on changes affecting the neighboring carbalkoxyl group itself. The base containing the carbmethoxyl group rearranges nearly twice as rapidly as the base in which a carbethoxyl group is substituted for the carbmethoxyl radical. And in the same way as a substitution of methyl for hydrogen in the para position to the amino group (5-methyl-2-aminophenyl ethyl carbonate) causes the greatest difference in the strength of the base (the affinity constant is doubled), so a substitution of methyl for hydrogen in the para position to the carbonate group (4-methyl-2-aminophenyl ethyl carbonate) in turn affects the velocity constant most decidedly—reducing it to one-third its original value.

PART II.

It was early felt that more extensive data would be desirable for determining the secondary influences which affect the rearrangement of *o*-aminophenyl alkyl carbonates, and after the main question had been decided affirmatively, that the substance undergoing rearrangement in the aqueous solutions of the salts is the free base, an extended study was made of the behavior of halogen derivatives of the bases. An unexpected difficulty was encountered in the fact that the hydrochloride of every halogen *o*-aminophenyl ethyl carbonate that was prepared proved to be insoluble in water. At first this was thought to be simply a peculiarity of the hydrochloride of 4-chloro-2-aminophenyl ethyl carbonate which was first prepared, and derivative after derivative was made with the hope of obtaining a soluble hydrochloride containing a negative group to compare with hydrochlorides containing the positive methyl group in the cresol series. The rearrangement had to be studied, therefore, in a mixture of alcohol and water ($1:1$), and we were obliged to restrict ourselves for the present to qualitative comparisons of the tendency of the halogen phenyl bases to rearrange. The comparisons are made by means of quantitative conductivity measurements, which will prove the basis for a future quantitative development of the question, as soon as the molecular conductivities, μ_v, of the non-hydrolyzed salts have been determined for the solvent used. They are necessary for distinguishing quantitatively the two factors which determine the actually observed rate of change in the solution, *viz.*, the degree of hydrolysis determining the concentration of the free base and the true velocity constant of the rearrangement of the base. The qualitative results will be given briefly in this part.

The basis for the qualitative comparisons by means of conductivity measurements is as follows :

The increase in the specific conductivity of a solution containing the hydrochloride of an *o*-aminophenyl ethyl carbonate is a measure of the increase in free hydrochloric acid, and this in turn is an approximate measure of the total rate of change ; it would be absolutely so if the salt were hydrolyzed accord-

ing to equation (1), just as fast as the base is destroyed. As explained before, this is not the case ; the acid is always liberated at a little slower rate than that at which the rearrangement proceeds. The difference is small, however, and particularly so when an excess of acid has already been formed by the rearrangement of 20 to 30 per cent of the salt ; the error, too, is always in the same direction and of the same order for bases, whose affinity constants are of the same order. These determine according to (1) the deviation from an exact ratio between the increase of acid and rate of rearrangement— while even a very large difference in the velocity constants has a smaller effect. Now, in the case of isomeric derivatives of *o*-aminophenyl alkyl carbonates, a like substitution in position 4 or 6, both meta to the basic amino group, has nearly the same effect on the affinity constants, as shown by a comparison of the bases V and VII in Table XVIII. Isomers which differ only in having position 4 or 6 occupied may, therefore, be compared with each other by this method. A substitution in position 5 (para to the amino group) always has a much more decided effect on the affinity constant (see VI in Table XVIII.), and we excluded this series of derivatives from this part of the investigation.

For the purpose of such comparison the proportion was determined between the observed change of the specific conductivity and the total increase in such conductivity for a complete rearrangement, and the time required for such a change was ascertained. The following table shows the qualitative comparison applied to the five bases which were studied quantitatively in Part I. and shows the applicability of the method as well as its limitations :

Table XIX.

	III.[1]			VII.			IV.			V.			VI.	
Per cent calc.	$t.$	Per cent obs.	$t.$	Per cent obs.	$t.$	Per cent obs.	$t.$	Per cent obs.	$t.$	Per cent obs.	$t.$	Per cent obs.		
25	38	33	51	33	50	31	208	36	77	32				
50	109	56	150	57	165	57	550	53	230	56				
75	270	77	380	78	375	79	1500	··	657	78				
85	450	87	596	85	590	87	···	··	···	··				

[1] The Roman numerals in this line represent the numbers and names of the bases as given in Table XVIII.

Column 1 gives the percentage of the total increase in conductivity taken as a measure of the percentage of change. The next division gives for 2-aminophenyl methyl carbonate (Base III, Table XVIII.) in the second column the time in minutes required to reach the stage specified in column 1, and in the third column the true percentage of change as determined quantitatively in Part I (see Table IV.). The same data are given for the other four bases in the subsequent divisions. It is at once apparent that measured by the time taken to reach the same degree of change (they are arranged in that order) all these bases fall into the same order, as they do according to their accurately ascertained velocity constants, with the exception of the last, 5-methyl-2-aminophenyl ethyl carbonate : in this case the para position to the amino group, position (5), is occupied and modifies so decidedly the affinity constant, that the method developed cannot be applied to it, as explained above. The table shows, then, that reliable qualitative comparisons of the tendency to rearrange may be made by this method, if isomers are compared which differ only in having position 4 or 6 (not 5), occupied.

The following table summarizes the results obtained with the halogen derivatives, giving the time in minutes required to rearrange 25, 50, 75, and 85 per cent of the bases in N/32 solutions of their hydrochlorides at 25°, in a mixture of alcohol and water (1 : 1) :[1]

[1] The amide hydrochlorides of this series are soluble in absolute alcohol and are not as a rule precipitated by the addition of an equal volume of water. They do not, however, go into solution readily when covered with a 50 per cent alcoholic solution. It was necessary, therefore, to dissolve them first in the alcohol and then to add the water. The heat generated when alcohol and water were mixed had to be taken into account. The method of proceeding which we adopted was as follows : A weighed amount which would give 50 cc. of a N/32 solution was dissolved in 25 cc. of absolute alcohol at 25°. Twenty-five cc. water which had been cooled to just 12° were then added and the vessel shaken for one-half minute in the water of a thermostat which was kept at 25° (±0°.01). The temperature of the solution at the end of this time was exactly 25°. This nearly 50 per cent alcoholic solution was then poured into the Arrhenius cell and the conductivity taken. From two to three minutes had in general elapsed before the first reading could be made.

Table XX.

No. of base.	Base.	Time required.			
		25 per cent.	50 per cent.	75 per cent.	85 per cent.
IV.	2-aminophenyl ethyl carbonate	7	19	35	51
VII.	2-amino-6-methylphenyl ethyl carbonate	8	26	54	85
V.	2-amino-4-methylphenyl ethyl carbonate	28	70	140	186
VIII.	2-amino-4-chlorphenyl ethyl carbonate	8	23	40	46
IX.	2-amino-6-chlorphenyl ethyl carbonate	2	4	8	12
X.	2-amino-4-bromphenyl ethyl carbonate	7	12	40	56
XI.	2-amino-4-methyl-6-bromphenyl ethyl carbonate	4	10	17	22
XII.	2-amino-4-brom-6-methyl-phenyl ethyl carbonate	..	..	43	57
XIII.	2-amino-4,6-dichlorphenyl ethyl carbonate	..	..	..	7[1]
XIV.	2-amino-4-chlor-6-bromphenyl ethyl carbonate	..	..	..	8[1]

The results given in the table lead to the following conclusions :

1. The methyl group in position (4) delays the rearrangement at 25°, as it does at 0° (compare base V with IV and VII).

2. At 25° a methyl group in position (6) retards the rearrangement somewhat—at 0° it caused a small acceleration (compare base VII and IV).

3. A halogen atom in position (6) always causes a very great increase in the velocity of the rearrangement, as compared with its effect in position (4) ; the relative velocity is, therefore, the same for the halogen derivatives as for the methyl derivatives.

4. A methyl group in position (4) retards the rearrangement also in the case of the halogen derivatives (compare IX and XI).

[1] 100 per cent.

5. The substitution of a halogen atom for hydrogen in position (4) of the aminophenyl or cresyl alkyl carbonates has a retarding effect on the velocity constant. The bases VIII, X, and XII are undoubtedly very much weaker bases[1] than aminophenyl ethyl carbonate (IV), and in consequence of the greater degree of hydrolysis of the hydrochlorides of the former bases their solutions would contain a much larger proportion of the free base. This would result in a far more rapid rearrangement, and a complete rearrangement in far shorter time, if the velocity constants were as large as that of aminophenyl ethyl carbonate (IV). The fact, therefore, that VIII, X, and XII require about the same length of time to reach the same degree of change as aminophenyl ethyl carbonate or, in fact, even a little more time than the latter, proves that their velocity constants must be smaller and probably considerably smaller than the latter. This is the most interesting result we found in this part of our work.

In conclusion it was possible to show that the substances undergoing rearrangement in the solutions of the salts of the halogen derivatives are again the free bases ; if the hydrolysis is partially suppressed by the preliminary addition of an excess of acid, the rearrangement is decidedly retarded, as shown by conductivity measurements with the hydrochloride of 4-chlor-2-aminophenyl ethyl carbonate. Whereas the experiments showed that the chloride is completely rearranged at 25° in eighty minutes in N/32 solution if there is no excess of acid added, in a N/32 solution containing an excess of 1 molecule of hydrochloric acid, complete rearrangement is effected at 25° only in two hundred and sixty minutes. It is this effect of an excess of acid which made it possible to prepare and isolate at all, the hydrochlorides of two bases, like dichlor- (XIII) and chlorbromphenyl ethyl carbonate (XIV), which, without the excess of acid, are completely rearranged in seven or eight minutes.

Chicago, April 23, 1903.

[1] This is not only to be expected from the effect of a halogen on the strength of bases, but it is proved by the fact that the total observed increase in conductivity is three times as large for base IV. as for the halogen derivatives mentioned.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE IONIZATION CONSTANTS OF PHENOL-PHTHALEIN, AND THE USE OF THIS BODY AS AN INDICATOR.

By H. N. McCoy.

The theory of indicators proposed by Ostwald[1] aims to explain the two most interesting and important phenomena observed in connection with these bodies: (1) the change of color, and (2) the great difference in sensitiveness of different indicators toward weak acids or weak bases. Quite recently Stieglitz[2] has called attention to the bearing of the chromophoric theory of the change of color of indicators, the evidence for which theory has been furnished chiefly by Bernthsen[3], and Nietzki and Burckhart[4], on Ostwald's views. It was there pointed out that although the change of color is, very probably, not the immediate consequence of the ionization of the salt of the indicator, the two (color change and ionization) are practically coincident. Indicators are always either weak acids or weak bases, and the change of color is always associated with the change of the indicator into its salt, or vice versa. Ostwald has made it appear very probable that the sensitiveness of an indicator is directly dependent upon its degree of ionization as acid or base. Stieglitz has shown that although the indicator may be a pseudo-acid, as the chromophoric theory supposes, Ostwald's theory of sensitiveness is still essentially correct. The ionization constant to be considered is then the apparent constant. This is in fact the product of the constant of the equilibrium between the pseudo- and the true acid, and the real ionization constant of the latter. Similar statements apply to basic indicators.

Accepting this theory of sensitiveness, a knowledge of the ionization constants of indicators becomes of prime importance for a scientific basis of acidimetry. Bredig[5] has also recog-

[1] Lehrbuch der allgemeinen Chemie, 1, 799 (1891); "Scientific Foundations of Analytical Chemistry," p. 118 (1895).
[2] J. Am. Chem. Soc., 25, 1112 (1903).
[3] Chem. Ztg., 1892, 1956.
[4] Ber. d. chem. Ges., 30, 175 (1897).
[5] Ztschr. Electrochem., 6, 33 (1899).

nized the advantage to be derived from a knowledge of such constants and has promised some work on methyl orange. So far as I know an account of this has not yet appeared.

The work which forms the basis of this paper was started three years ago in connection with a study of the equilibrium between the carbonates of sodium, carbon dioxide, and water.[1] In titrating sodium carbonate solutions, phenolphthalein being used as indicator, it became apparent that the amount of acid required to discharge the color of the alkaline solution depended upon the amount of the indicator used ; that, in fact, a state of equilibrium existed in which the concentration of the phenolphthalein was one of the factors.

In consequence of this view, it was thought that by determining the ionization constant of phenolphthalein, as an acid, a colorimetric method might be applied to determine the degree of alkalinity of solutions of sodium bicarbonate. It was found experimentally, that the addition of the calculated quantity of pure barium hydroxide to a very dilute aqueous solution of phenolphthalein developed but a fraction of the color given by the same quantity of phenolphthalein with excess of alkali. This effect was supposed to be due chiefly to hydrolytic dissociation, and it was thought that the degree of hydrolysis could be determined by colorimetric measurements, by using for comparison phenolphthalein solutions containing an excess of alkali. As phenolphthalein is a weak acid, we should have as the dynamic equation of ionization :

$$H \times Q = K_1 \times L, \qquad (1)$$

where H and Q represent the concentrations of the hydrogen and negative ions respectively, and L that of the non-ionized substance. By combining this equation with that of the ion-product of water, $H \times OH = K_{H_2O}$ we get

$$\frac{L \times OH}{Q} = \frac{K_{H_2O}}{K_1} = K, \text{ a constant.} \qquad (2)$$

If the acid is weak, as is the case with phenolphthalein, and the base is highly ionizable, this equation becomes identical with the familiar one of Walker :[2]

[1] This JOURNAL, **29**, 437 (1903).
[2] Ztschr. phys. Chem., **4**, 324 (1889).

$$\frac{\text{acid} \times \text{base}}{\text{salt}} = \text{a constant.}$$

The method tried consisted in adding $N/200$ barium hydroxide in known amounts, to 100 cc. of a $N/12,000$ phenolphthalein solution, which was made by dissolving chemically pure phenolphthalein in pure, freshly boiled water contained in a platinum dish. The concentration of salt formed was determined colorimetrically. The comparison solution was made by adding the requisite volume of $N/12,000$ phenolphthalein and one cc. of normal sodium hydroxide to sufficient water to make 100 cc. The solutions were compared in 100 cc. Nessler cylinders. Owing to the great excess of alkali in the comparison solution, the hydrolysis was so slight (see p. 512) that the total concentration of the phenolphthalein could be considered equal to that of the salt in the other solution of the same intensity of color. Table I. gives the results obtained. In each experiment 100 cc. of $N/12,000$ phenolphthalein were used. Column 1 gives the volume of $N/200$ barium hydroxide added. The ratio of total alkali to total phenolphthalein was varied from 1 : 1, first experiment, to 4 : 1, last experiment. The second column gives the volume of $N/12,000$ phenolphthalein required for the comparison solution. It also expresses the percentage of phenolphthalein converted into salt by the barium hydroxide. The last column gives the value of the hydrolysis constant, K, as calculated by means of equation (2). Since the ionization of a salt is almost complete in these very dilute solutions, Q, the concentration of the negative ions, may be considered practically equal to that of the red salt. L is equal to the total concentration of the indicator minus Q, and OH to the total concentration of barium hydroxide minus Q.

Table I.

$Ba(OH)_2$. cc.	Phenolphthalein. cc.	$10^4 K$.
1.7	8	8.8
3.4	35	2.6
5.1	54	1.7
6.8	80	0.7

These results were so far from satisfactory that the work was discontinued at that time.

The variability of K is to be ascribed chiefly to two causes: First, the presence of impurities in the distilled water, the most important being carbon dioxide; and, second, the fact that the indicator contains two phenol groups. The latter as well as the former would, by union with the alkali added, reduce the available base concentration. To avoid these difficulties a method was employed which readily gave a known hydroxyl concentration, irrespective of the presence of small amounts of acid impurities in the water, and of the phenol groups. This was done by using a rather large amount of a weak base, ammonia, in the presence of a known amount of one of its salts. An example will illustrate the idea. Suppose 2 cc. of $N/10$ ammonia, 10 cc. of $N/10$ ammonium chloride, and 0.05 cc. of $N/10$ phenolphthalein be added to sufficient water to give 100 cc. The concentration of the base employed would be 2000×10^{-6}, that of the indicator 50×10^{-6}, and that of the carbon dioxide present in the water[1] about 10^{-5}. If the phenolphthalein neutralizes one *extra* equivalent of base, on account of the phenol groups, and if the carbon dioxide is also neutralized, the amount of ammonia is not appreciably diminished. The hydroxyl concentration is readily calculated from the equation $NH_4 \times OH = 23 \times 10^{-6} \times NH_4OH$.[2] If neither phenolphthalein nor carbon dioxide is present, $OH = 4.6 \times 10^{-6}$, while in the above case $OH = 4.5 \times 10^{-6}$. This small difference may be neglected. Owing to the fact that the acid and acid groups are weak, the degree of hydrolysis would be great, so that the actual amount of base neutralized in this way would be much less than the above estimate. The hydroxyl concentration is also somewhat diminished in other ways. By taking these into account a more accurate value of the hydroxyl concentration may be found. Let the total concentrations of ammonium hydroxide and ammonium chloride used be represented by B and S, respectively, and call the

[1] McCoy: This JOURNAL, **29**, 457 (1903).
[2] Bredig: Ztschr. phys. Chem., **13**, 284 (1894).

concentration of the red salt formed, Q. For the state of equilibrium the concentration of the molecular ammonium hydroxide is less than B by the amount converted into the red salt, Q, plus the amount existing as ammonium and hydroxyl ions, and, of course, equivalent to the latter in concentration. Therefore, $NH_4OH = B - (Q + OH)$. The ammonium ions come chiefly from the ammonium chloride, but the concentration is increased by the amount of red salt, Q, plus the amount of the ionized ammonium hydroxide, OH. Therefore

$$NH_4 = S + Q + OH,$$

and since

$$OH = \frac{23 \times 10^{-6} \times NH_4OH}{NH_4},$$

$$OH = \frac{23 \times 10^{-6}(B - Q - OH)}{S + Q + OH}. \tag{3}$$

In deducing this equation it has been assumed that the salts are completely ionized, and that the effect on the hydroxyl concentration of phenol groups and of impurities in the water may be neglected. The hydrolysis constant of phenolphthalein may then be calculated, as in Table I., by means of the equation:

$$L \times OH = K \times Q, \tag{2}$$

by substituting for the factor OH, the value as calculated above.

The first step toward the testing of these deductions was the preparation of pure phenolphthalein. Commercial phenolphthalein is quite impure. It was readily freed from all impurities as follows: The yellow powder was treated with 1.5 volumes of cold methyl alcohol and allowed to stand several hours. It was then filtered and washed with cold methyl alcohol. This removed a large part of the yellow resinous matter. The light colored residue was dissolved in boiling methyl alcohol and the solution evaporated until it was of 25 to 30 per cent strength. Upon adding a crystal of phenolphthalein, cooling, and shaking, white crystals of the pure substance were obtained. The yield was very good.

The preparation of a solution of phenolphthalein presented some difficulties. Menschutkin,[1] and also Jones and Allen,[2] have observed that dilute ammonia in small quantity does not color an alcoholic solution of phenolphthalein. Schmatolla[3] has found that an alcoholic solution of phenolphthalein,[4] colored pale-red by a small amount of sodium hydroxide becomes intensely red upon the addition of much pure water. I have also observed that a very dilute aqueous solution, containing equivalent amounts of barium hydroxide and the indicator, is perceptibly bleached by the addition of even small quantities of alcohol. This effect was shown to be due to pure alcohol, free from all traces of acid. Some pure absolute alcohol (Kahlbaum) was rendered slightly alkaline by the addition of a few drops of a solution of barium hydroxide and then distilled, using a 15-inch fractionating-tube. Two cc. of the middle portion of the distillate were added to 100 cc. of a N/20,000 phenolphthalein solution containing an equivalent amount of barium hydroxide. The color of the solution was reduced to about half its original intensity ; 0.4 cc. of alcohol added to another 100 cc. portion bleached it quite perceptibly, while 0.1 cc. of alcohol produced a scarcely noticeable effect on the color of a third portion.[5] From these results it was evident that appreciable quantities of alcohol could not be used in making up the phenolphthalein solutions to be studied.

A decinormal phenolphthalein solution was made by dissolving 3.18 grams of the substance (0.01 mol.) in sufficient pure alcohol (freshly distilled from barium hydroxide) to give a volume of 100 cc. 0.05 cc. of this solution added to 100

[1] Ber. d. chem. Ges., **16**, 315 (1883).
[2] This JOURNAL, **18**, 377 (1896).
[3] Ber. d. chem. Ges., **35**, 3905 (1902).
[4] Waddel : J. Phys. Chem., **2**, 176 (1898).

[5] The theory of Jones and Allen that a smaller degree of ionization in alcoholic solutions produces the observed effects, can (even supposing the ionization theory of indicators to be correct) scarcely apply to such dilute alcoholic solutions as I have used. The cause of the bleaching might possibly be ascribed to the possession of very weak acid properties by the alcohol. But Kullgren (Ztschr. phys. Chem., **37,** 614 (1901)) has determined the velocity of saponification of methyl acetate in the presence of an excess of alcohol and found evidence that alcohol has not even faint acid properties. The cause of the action of alcohol, is, therefore, still an open question.

cc. of water gave a N/20,000 solution.[1] The standard ammonium hydroxide was prepared from a solution freshly distilled from a little barium hydroxide, in order to remove the carbonate.

The experimental process consisted in adding to about 80 cc. of pure water, contained in a Nessler cylinder, successively ammonia, phenolphthalein, and ammonium chloride, each in decinormal solution. Sufficient water was then added to give a total of 100 cc. The cylinder was stoppered, to avoid absorption of carbon dioxide, and the contents completely mixed. The comparison solution was made and used as previously described (p. 505).

In Tables II., III., IV., and V. are given the results obtained with solutions N/20,000 with respect to phenolphthalein. The fourth column gives the volume of N/20,000 phenolphthalein which, when mixed with 1 cc. of normal sodium hydroxide and sufficient water to make 100 cc., was necessary to match the color of the solution being studied. It gives also the percentage of the indicator which is converted into the red salt, in the corresponding ammoniacal solution. The fifth column gives the hydroxyl concentration as calculated by means of equation (3). The last column gives the value of the hydrolysis constant.

Table II.

	N/10 NH$_4$OH. cc.	N/10 NH$_4$Cl. cc.	N/20,000 Phenolphthalein. cc.	10^6 OH.	10^4 K.
1	2	1	36.0	42.0	0.8
2	2	2	20.0	22.0	0.9
3	2	10	3.2	4.6	1.4
4	2	20	1.4	2.3	1.6
5	2	40	0.6	1.2	2.0
				Average,	1.34

Solution 5 was rendered colorless by the addition of 0.4 cc. of N/10 hydrochloric acid.

[1] In measuring the small volumes of the solutions Meineke burettes (Centrbl., 1892, II., 193) were used. The small tube, having a total capacity of 2 cc., was graduated in hundredths of a cubic centimeter, so that it was possible to measure with fair accuracy to within 0.001 cc.

Table III.

	N/10 NH$_4$OH. cc.	N/10 NH$_4$Cl. cc.	N/20,000 Phenol-phthalein. cc.	10^6 OH.	10^4 K.
1	1	0.5	30.0	39.0	0.9
2	1	1.0	15.0	21.7	1.2
3	1	5.0	2.5	4.6	1.7
4	1	10.0	0.9	2.3	2.3
5	1	20.00	Colorless	1.2	··
				Average,	1.53

Table IV.

	N/10 NH$_4$OH. cc.	N/10 NH$_4$Cl. cc.	N/20,000 Phenol-phthalein. cc.	10^6 OH.	10^4 K.
1	0.5	0.2	30.0	40.0	0.9
2	0.5	0.5	15.0	20.0	1.0
3	0.5	1.0	8.0	9.8	1.0
4	0.5	2.0	3.3	5.7	1.6
5	0.5	5.0	0.8	2.3	2.8
6	0.5	10.0	Colorless	1.2	··
				Average,	1.46

Table V.

	N/10 NH$_4$OH. cc.	N/10 NH$_4$Cl. cc.	N/20,000 Phenol-phthalein. cc.	10^6 OH.	10^4 K.
1	0.3	0.1	24.0	38.0	1.2
2	0.3	0.3	11.0	19.5	1.6
3	0.3	0.4	10.0	15.3	1.4
4	0.3	1.0	3.8	6.7	1.9
5	0.3	3.0	0.8	2.3	2.8
6	0.3	6.0	Colorless	1.2	··
				Average,	1.78

The average of all experiments of Tables II. to V. is K = 1.53 × 10^{-4}.

The very slight solubility of phenolphthalein in pure water limited the study of the hydrolysis of its salts to extremely dilute solutions. So far as I am aware, the solubility of phenolphthalein has not been accurately determined. Approximate determinations were made by two methods. In the first 0.0318 gram (0.0001 mol.) was boiled with water. Twelve hundred cc. were required to dissolve this amount. The solution on cooling did not form a deposit. This solu-

tion was N/12,000. The second method consisted in adding to 100 cc. of N/500 ammonia known volumes of alcoholic N/10 phenolphthalein. The resulting clear solutions were each neutralized by the addition of 2 cc. of N/10 hydrochloric acid. With 0.5 cc. N/10 phenolphthalein a white precipitate formed when the solution was neutralized. With 0.3 cc. the solution was turbid, with 0.2 cc. the solution was faintly turbid, while with 0.1 cc. the solution remained clear upon neutralization, but formed a slight precipitate on standing over night. The last solution, which was evidently slightly supersaturated, was N/10,000. This concentration therefore represents the maximum that may be employed in volumetric work.

In Table VI. are given the results of a series of experiments with solutions containing N/10,000 phenolphthalein. The number of cubic centimeters of N/20,000 phenolphthalein required to make the comparison solution (fourth column) is now equal to twice the percentage of red salt formed.

Table VI.

	N/10 NH$_4$OH. cc.	N/10 NH$_4$Cl. cc.	N/20,000 Phenol-phthalein. cc.	10^6 OH.	10^4 K.
1	0.5	0.5	35.0	19.8	0.94
2	0.5	0.5	30.0	20.0	1.13
3	0.5	2.0	6.0	5.6	1.81
4	0.5	2.0	7.0	5.6	1.55
5	0.5	5.0	1.7	2.3	2.7
6	0.5	5.0	1.6	2.3	2.9
7	2.0	2.0	50.0	22.0	0.66
8	2.0	10.0	9.0	4.6	0.98
				Average,	1.58

From the first series of experiments, $K = 1.53 \times 10^{-4}$; from the second series, $K = 1.58 \times 10^{-4}$. The mean is 1.55×10^{-4}, or roundly 1.6×10^{-4}. The ionization constant of phenolphthalein, considered as an acid, being called K_1, we have

$$K_1 = \frac{K_{H_2O}}{K}.$$

The ion product of water[1], $K_{H_2O} = 1.2 \times 10^{-14}$. Therefore,

[1] Van 't Hoff : "Vorlesungen über theoretische und physikalische Chemie," I, 124 (1901).

$K_1 = 7.5 \times 10^{-11}$. The degree of hydrolysis of the red salt in N/100 sodium hydroxide (the concentration used in the comparison solutions) may be calculated from these figures:

$$L \times OH = 1.6 \times 10^{-4} Q;$$

$$OH = 10^{-2}.$$

Therefore $L = 1.6 \times 10^{-2}Q$; or the hydrolysis equals 1.6 per cent. This small amount may be neglected.

The Use of Phenolphthalein as an Indicator.—The chief value to be derived from a knowledge of the ionization constant of an indicator lies in the fact that it is easy to calculate, by means of this constant, the degree of accuracy with which it is possible to titrate any acid or base of known ionization constant. This may be done by considering the end-point of the reaction from the standpoint of chemical equilibrium.

The minimum concentration of the red salt of the indicator required to give to 100 cc. of alkaline water a barely perceptible color was determined. It was found that 0.4 cc. of an N/20,000 phenolphthalein solution gave to 100 cc. of N/100 sodium hydroxide a barely visible color. This solution was 2×10^{-7} normal with respect to phenolphthalein. An alkaline solution containing less than this concentration of the indicator could not be distinguished from pure water. The minimum hydroxyl concentration detectable by means of N/20,000 indicator may be calculated from the equation

$$acid \times base = K \times salt.$$

Acid $= 5 \times 10^{-5}$. Salt $= 2 \times 10^{-7}$. The average value of $K = 1.6 \times 10^{-4}$; but as the values found for solutions which were very nearly neutral were, for some reason not apparent, somewhat greater than the average, it is perhaps better to take as the value of this constant the mean of the last values found in each series of experiments, as more nearly representing the conditions existing in actual titrations. This is $K = 2.5 \times 10^{-4}$. Therefore

$$OH = \frac{2.5 \times 10^{-4} \times 2 \times 10^{-7}}{5 \times 10^{-5}} = 10^{-6}.$$

This is very near the mean value of OH in the last experiments of Tables II. to V., for solutions which were barely colorless. It follows from this, that in titrating acids, in order that the end-point may be just colorless, the hydroxyl concentration must be 10^{-6}. Since $H \times OH = 1.2 \times 10^{-14}$, H must equal 1.2×10^{-8}. That is, for a barely colorless solution OH must equal 80 H. If OH is greater than 80 H the solution will be perceptibly red.

By means of the data just obtained the minimum error involved in the titration of a weak acid, HA, of ionization constant, k_a, may be calculated. In such a case

$$H \times A = k_a HA$$
$$\frac{H}{k_a} = \frac{HA}{A}.$$

Now, for the neutralized solution (that is, at the end of the titration) A is practically equal to the total concentration of the salt, since ionization in the dilute solution will be nearly complete. The concentration of the acid not neutralized is equal to $H + HA$; but $H = 1.2 \times 10^{-8}$, and is therefore so small as to be negligible. HA/A is practically the fraction of the original acid not neutralized. It is therefore the error, E_a, of the analysis

$$E_a = \frac{H}{k_a} = \frac{1.2 \times 10^{-8}}{k_a}.$$
$$k_a = 1.2 \times 10^{-8}/E_a. \qquad (4)$$

By means of the last equation one may calculate the ionization constant of an acid which may be titrated with a given error of analysis. (It is here assumed that the volume is about 100 cc. at the end of the titration and that the concentration of the phenolphthalein is N/20,000.) If E_a is 0.1 per cent, k_a is equal to 1.2×10^{-5}. For $E_a = 0.2$ per cent $k_a = 0.6 \times 10^{-5}$. Ostwald[1] has determined the ionization constants of a large number of organic acids. In the list of over 200 acids only eight have an ionization constant less than 1.2×10^{-5}, and for four of these the value is greater than

[1] Ztschr. phys. Chem., **3**, 418 (1889).

0.6×10^{-5}. The constants of the fatty acids (excepting formic acid, which is quite strong) all lie between 1.2×10^{-5} and 1.8×10^{-5}, acetic acid having the latter value. It should therefore, be possible to titrate, with analytical accuracy, all such acids. This conclusion is fully confirmed by common experience. Phenolphthalein is consequently an excellent indicator for almost all acids, including the so-called weak acids.

The results to be expected in the titration of a weak base, MOH, by means of a strong acid may be calculated in an analogous manner. In this case $M \times OH = k_b MOH$,

and
$$\frac{OH}{k_b} = \frac{MOH}{M}.$$

After the addition of acid to the solution of the base until the disappearance of color indicates neutrality, the fraction MOH/M expresses the error, E_b, of the titration. Since $OH = 10^{-6}$.

$$k_b = 10^{-6}/E_b. \tag{5}$$

For an error of 0.1 per cent, k_b should be equal to 10^{-3}; for 0.2 per cent, 0.5×10^{-3}. The ionization constants of 30 organic bases have been measured by Bredig.[1] In addition to very strong bases of the quaternary ammonium type, 21 others were studied. Only four of these have constants over 10^{-3}. These are diethylamine, dipropylamine, coniïn, and piperidine. These could be titrated accurately with phenolphthalein as indicator. Thirteen more, mostly aliphatic amines, have constants between 10^{-3} and 0.5×10^{-3}. These could be titrated with a fair degree of accuracy. The constant for ammonia is 0.023×10^{-3}. The error of titration would be about 4 per cent. In the last experiments of Tables II. to V. the solutions became colorless when the concentration of the free ammonia was about 4 per cent of the concentration of the salt. It is, of course, evident that this last fact was used in arriving at the above conclusions. By combining the equations representing the relation between ionization constants and errors of analysis we get for the case where $E_b = E_a$

[1] *Loc. cit.*

$$\frac{k_b}{k_a} = \frac{OH}{H} \qquad (6)$$

and for $k_b = k_a$

$$\frac{E_b}{E_a} = \frac{OH}{H}. \qquad (7)$$

The first of these equations shows that for the same error of analysis of base and acid the ratio of the ionization constants of base and acid must be the same as that of the minimum detectable concentrations of hydroxyl and hydrogen. The second equation shows that if base and acid have equal ionization constants, the errors of analysis are in the same ratio as that of minimum detectable hydroxyl to hydrogen. The equations are applicable to indicators in general. The ratio OH to H will be characteristic for each indicator. For phenolphthalein it has been shown to be about 80. It is well known that this substance is a poorer indicator for weak bases than for weak acids. The quantitative relationship is given by these equations. While for the accurate titration of the weakest bases phenolphthalein could not be used as an indicator, it could be so used with many of the amines and other moderately weak bases.

Since it is possible by means of phenolphthalein to detect hydroxyl in concentration as small as 10^{-6}, it should be found that those alkali or alkali earth salts of weak acids, which by hydrolysis, give solutions exceeding in alkalinity this minimum hydroxyl concentration, should be alkaline toward phenolphthalein. Sodium acetate in decinormal solution is hydrolyzed to the extent of 0.01 per cent.[1] In this solution $OH = 10^{-5}$. Experiment 3, Table V, shows that 100 cc. of such a solution, plus 0.05 cc. N/10 phenolphthalein, should have a color equivalent to that produced by 8 cc. of N/20,000 phenolphthalein contained in 100 cc. of alkaline water. An experiment made with pure, carefully recrystallized, sodium acetate, gave a result in harmony with this deduction. The color of the solution was distinctly red. Lellmann[2] proposed the use of phenolphthalein to determine the relative affinities

[1] Shields : Ztschr. phys. Chem., **12**, 184 (1893).
[2] Ber. d. chem. Ges., **22**, 2101 (1889).

of weak acids, but has not used it[1] on account of its extreme weakness as an acid and the possibility of complications which might arise from the presence of the phenol groups. However, the method may be of some use as a means of determining rapidly the approximate affinities of acids whose salts are slightly hydrolyzed.

In the case of salts of weak dibasic acids, I have shown[2] that the degree of hydrolysis is much less than one might expect from the conductivity of the free acid.[3] The hydroxyl concentration of a decinormal solution of sodium bicarbonate is 3×10^{-6} (this is but 1/20 of the value calculated in the ordinary way from the conductivity measurements of carbonic acid). A hydroxyl concentration of 10^{-6} is the minimum detectable by means of phenolphthalein. In agreement with this Küster[4] has found as the result of very careful experiments that a *freshly made, dilute* solution of pure sodium bicarbonate is slightly alkaline toward phenolphthalein. (Owing to loss of carbon dioxide, such a solution becomes strongly alkaline on standing in an open vessel.[5]) I can confirm Küster's statement. The color of the solution is quite faint and depends upon the amount of the indicator used. The color may not appear if the water used be not free from carbon dioxide, or if an alcoholic solution of the indicator be employed, especially if the alcohol be not perfectly pure.

The Bleaching of Phenolphthalein by an Excess of Alkali.— It is well known that the addition of a very large excess of alkali to a slightly alkaline solution of phenolphthalein causes a great diminution in color. The results obtained in a series of experiments, made by mixing the indicator and sodium hydroxide in known amounts, are given in Table VII. Columns 2 and 3 give the concentrations used of phenolphthalein and sodium hydroxide respectively. In column 4 is given the volume of alkaline N/20,000 phenolphthalein required to match the color of the solution being studied. These figures

[1] Ann. Chem. (Liebig), **270**, 204 (1892).

[2] This JOURNAL, **29**, 452 (1903).

[3] Walker : Ztschr. phys. Chem., **32**, 137 (1900).

[4] Ztschr. anorg. Chem., **13**, 127 (1897).

[5] McCoy : *Loc. cit.*

therefore represent the percentages of the red salt which have remained unbleached.

Table VII.

	10^6 Phenol-phthalein.	10^2 NaOH.	N/20,000 Phen-olphthalein. cc.	10^3 K_3.
1	50	1	56.0	12
2	50	5	15.0	9
3	50	10	7.3	8
4	50	20	3.1	6
5	50	50	1.1	6
				—
			Mean,	8

As a possible explanation of the bleaching, it may be supposed that the red salt is also an *extremely weak* acid, which is converted into the corresponding colorless salt only by the addition of a great excess of base. In such a case the value of $\dfrac{\text{acid} \times \text{base}}{\text{salt}}$ should be a constant. Here the red salt is the *acid* and the colorless body the *salt*. The results calculated on this basis are given in the last column.

A deeper insight into the nature of the whole problem of the action of bases on phenolphthalein may be obtained by considering the various reactions from the standpoint of the graphical formulas of this indicator and of its salts. Solid phenolphthalein is very probably a lactone.[1]

$$C_6H_4{<}{\begin{matrix}CO\\C\end{matrix}}{>}O \qquad\qquad L$$
$$\overset{\|}{(C_6H_4OH)_2}$$
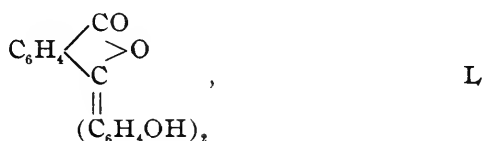
while the red salt and its corresponding free acid are quinone derivatives of the constitution

$$C_6H_4{<}{\begin{matrix}COOH\\C\end{matrix}} = C_6H_4 = O. \qquad HQ$$
$$\overset{|}{C_6H_4OH}$$
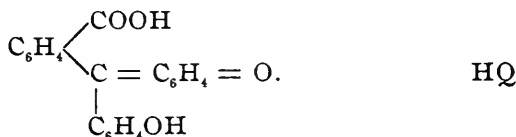
[1] Bernthsen : *Loc. cit.;* Nietzki and Burckhart : *Loc. cit.*

In aqueous solution the lactone, L, and the quinone carboxylic acid, HQ, would exist in equilibrium. The free acid, in turn, would be in equilibrium with its ions. For these reactions we should have as the obvious dynamic equations :[1] $L = k_1HQ$ and $H \times Q = k_2HQ$ (considering only the ionization of the carboxylic acid group), and therefore $H \times Q = k_1k_2L = K_1L$, where $K_1 = k_1k_2$. The value of K_1 has been found to be 7.5×10^{-11}. k_2 is the ionization constant of a substituted benzoic acid. The constant of benzoic acid is 6×10^{-5} and it may be supposed that k_2 is of the same order. If so, k_1 is equal approximately to 10^{-6}. This would mean that the concentration of the molecular quinoid carboxylic acid, HQ, is but one-millionth of that of the lactoid form.

The evidence for the constitution of the colorless salt, formed by the action of a great excess of sodium hydroxide, is of an indirect nature, but leads to the structural formula

$$C_6H_4 \begin{cases} COONa \\ C-OH \\ \| \\ (C_6H_4ONa)_2 \end{cases} \qquad I$$
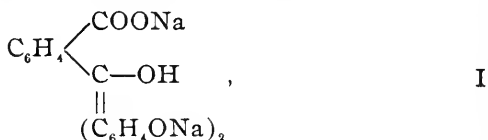
which represents a carbinol derivative. In this colorless salt the chromophoric quinone group is thought to be absent. In dilute solution the red salt would exist chiefly as ions, Q, which according to the above view would be

$$C_6H_4 \begin{cases} CO\overline{O} \\ C = C_6H_4 = O. \\ | \\ C_6H_4\overline{O} \end{cases} \qquad Q$$
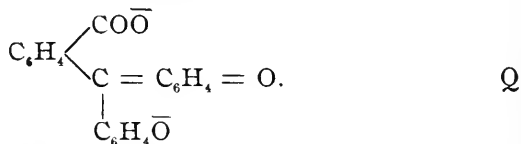
The formation of the carbinol derivative from this is to be represented by the equation, $Q + H_2O \rightleftharpoons HC$, where HC represents

$$C_6H_4 \begin{cases} CO\overline{O} \\ COH \\ \diagup \quad \diagdown \\ C_6H_4\overline{O} \quad C_6H_4OH* \end{cases} \qquad HC$$
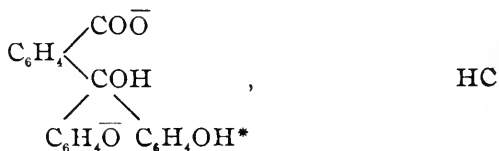
[1] Stieglitz : *Loc. cit.*

the carbinol ion-acid corresponding to the colorless salt. The body, HC, being an acid, due to the hydrogen atom, H*, we should have HC $\leftrightarrows$ C + H. The corresponding dynamic equations are HC = k_3Q and C $\times$ H = k_4HC. Therefore, C $\times$ H = k_3k_4Q = K_2Q, where $K_2 = k_3k_4$. In other words Q would be a pseudo-acid[1] and its salts would have a hydrolysis constant, K_3, equal to K_{H_2O}/K_2. The value of K_3 has been found to be 8 $\times$ 10^{-3} (Table VII.). Therefore $K_2 = 1.5 \times 10^{-12}$. k_4 is the ionization constant of a substituted phenol. For the common phenol Walker and Cormack[2] have found the ionization constant to be 1.3 $\times$ 10^{-10}. If k_4 is of the same order, as is likely the case, k_3 would be about 10^{-2}. The equilibrium reactions of the bleaching are accordingly analogous to those representing the formation of the red salt : the equilibrium constant in each case is the product of two other constants. In the case of the formation of the red salt the equilibrium constant, k_1, is small and the ionization constant, k_2, comparatively large. In the other case the reverse is true: the equilibrium constant is large and the ionization constant is extremely small.

It would not have been possible to have carried out the work described in this paper, except for the fact that the bleaching reaction takes place very slowly. In Experiment 1, Table VII, the velocity of the change was roughly measured. After ten minutes the bleaching amounted to about 10 per cent ; after fifty-four minutes to about 25 per cent ; after twenty-four hours to 43 per cent ; and after three days to 44 per cent. The alkaline phenolphthalein solutions used for the color comparison contained alkali of the same concentration as that used in this experiment. As these comparison solutions were made up only immediately before using, the fading which took place during the two or three minutes of use could be neglected. This observation on the velocity of bleaching clearly shows that we are dealing with a reaction which results in a condition of equilibrium, inasmuch as after the first day no further change occurred. The possibility of

[1] Hantzsch : Ber. d. chem. Ges., **32**, 579 (1899).
[2] J. Chem. Soc. (London), **77**, 5 (1900).

a non-reversible decomposition of the indicator is therefore excluded. In accord with this, it is found that upon diluting bleached solutions of phenolphthalein in concentrated alkali, the color becomes more intense. When the solution is neutralized with acetic acid and then immediately made slightly alkaline the solution has but a faint pink tint; but if the acid solution be boiled and then made slightly alkaline the intense red color appears. Green[1] thinks that this is evidence that the cause of the change of color is intramolecular instead of essentially ionic. I have carried out an experiment which throws additional light on this question. About 0.1 gram of pure phenolphthalein was dissolved in 10 cc. of N sodium hydroxide. After standing until equilibrium was reached, the deep-red solution was rendered just colorless by the addition of acetic acid. A slight precipitate formed, but much the larger part of the substance remained in solution. On standing at room temperature the colorless, and therefore *neutral* solution soon became somewhat red, the color gradually growing more intense; after an hour or two the solution was deep red. A considerable volume of dilute acetic acid was then required to again neutralize the solution, the unchanged phenolphthalein itself serving as indicator.

The result just described is welcome confirmatory evidence of the views here expressed on the constitutions of phenolphthalein derivatives, and on their dynamic relationships. The change of Q into HC takes place slowly, as the fading experiments show. The action is reversible and reaches a state of equilibrium. As has been said, a red solution of phenolphthalein, in dilute sodium hydroxide, probably contains the salt of a carboxylic acid of constitution HQ. Now aromatic carboxylic acids, in general, are *not* extremely weak acids. They are stronger than acetic acid. But in this case, owing to the fact that the corresponding free acid can go practically *instantaneously* and almost completely into the lactone, the *observed* properties are those of a very weak acid whose ionization constant is the product of k_1 and k_2.

On the other hand, the colorless salt, formula I, is also the

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[1] Ztschr. f. Farb. u. Tex. Chem., **I**, 413; Chem. Centrbl., 1902, II, 683.

salt of a carboxylic acid, but in this case the reversion to the tautomeric form *takes place slowly;* that is to say, the change, $Q \rightleftarrows HC$ does *not* take place instantly. It should, therefore, be possible, under favorable conditions, to observe properties characteristic of an aromatic carboxylic acid. Upon adding acetic acid to the strongly alkaline, bleached solution, until it became colorless, a neutral solution was obtained, which, on standing, became strongly alkaline. The neutral solution must have contained the salt of a moderately strong acid. The alkaline solution, spontaneously formed from the preceding, contained the ordinary red salt of phenolphthalein. The neutral salt was probably

$$C_6H_4 \Big\langle \begin{matrix} COONa \\ C{-}OH \\ || \\ (C_6H_4OH)_2 \end{matrix} \qquad . \qquad \qquad II$$
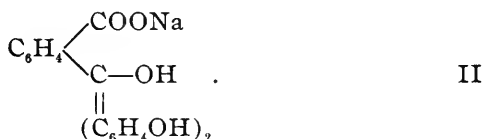
But if this substance can transform *slowly* into the salt of HQ, which acid is *practically very weak*, the results obtained are easily understood. The solution of the latter salt would, of course, owing to hydrolysis, be strongly alkaline. Further, as a result of the competition of the phenol groups of II, a portion of the alkali of the salt of HQ would neutralize the former and thus convert II partly into I. This would tend to diminish the velocity of transformation of II into the red quinoid form (salt of HQ).

Chicago, January, 1904.

THE HYDROLYSIS OF ETHYL BUTYRATE BY LIPASE.

By J. H. Kastle, Marius Early Johnston, and Elias Elvove.[1]

During the summer of 1900, an experimental study of the action of lipase on certain ethereal salts was carried out in this laboratory by Loevenhart and one of us. The results of this investigation have already been published in this JOURNAL.[2] Among other things it was found that as compared with other

ethereal salts, ethyl butyrate is very easily hydrolyzed by lipase, so readily in fact as to render it an exceedingly useful substance in the investigation of a number of problems connected with the action of this ferment.

Clear Solutions of Lipase.

It was also observed in our earlier work that filtration greatly diminishes the activity of the enzyme. To such an extent was this found to occur that at that time no attempts were made to obtain the ferment in anything like a condition of purity, nor even in the form of water-clear solutions. It was apparent, however, even from the outset, that clear and homogeneous solutions of the enzyme must be obtained before we could hope to accurately investigate certain phases of the lipolytic process. Some time after this, in studying the conduct of acids towards lipase, it was observed by Kastle and Hardin[1] that when 10 per cent extracts of hepatic lipase were allowed to stand with small amounts of $N/100$ hydrochloric acid a certain amount of proteid is coagulated, and when this extract is filtered, a clear, yellowish filtrate is obtained, which is found to possess considerable lipolytic activity. Upon this observation is based the following methods for the preparation of clear solutions of hepatic lipase :

Ten grams of fresh hog liver were thoroughly macerated with coarse white sand and made up to 100 cc. with water, and strained through a linen cloth. Twenty cc. of this extract were then diluted with 72 cc. of water and to the diluted extract 8 cc. of $N/100$ hydrochloric acid were added, and the mixture heated to 40° C. Under these conditions a heavy albuminous precipitate was thrown down. This was then filtered off and a clear filtrate obtained, having a light, golden-yellow color. The lipolytic activity of this solution before and after filtration was tested in the following manner :

Four tubes were prepared, two containing 5 cc. of the unfiltered solution and two containing 5 cc. of the filtered solution. To each of the tubes 0.1 cc. of toluene was added as antiseptic, and the tubes were heated on the water-bath at 40°

[1] Unpublished results of Kastle and Hardin.

C. for five minutes. 0.26 cc. of ethyl butyrate was then added to each tube, after which the tubes were allowed to remain in the bath for fifteen minutes. They were then removed from the bath and placed in ice-water and titrated with N/20 caustic soda with the following results :

		N/20 NaOH required.	Percentage of hydrolysis.
Unfiltered solution		5.05	12.67
"	"	5.25	13.1
Filtered	"	2.75	6.89
"	"	3.00	7.53

From this it will be observed that in the preparation of clear lipase solution there is a falling off in activity of nearly one-half as compared with the original extracts. However, the activity of such clear solutions is still considerable, and the advantages of such solutions over the turbid aqueous extracts for the purposes of chemical study can scarcely be overestimated. In order to determine the amount of solid matter in these clear solutions of lipase, 5 cc. of such a solution were evaporated to dryness in a platinum dish over the water-bath, and dried to constant weight in the air-oven at 100° C. The residue was found to weigh 0.0104 gram. The residue was then ignited and weighed again. The mineral matter was found to weigh 0.0016 gram. It will be observed, therefore, that even on the assumption that the whole of the organic matter consists of lipase, and this is by no means probable, it can hydrolyze twice its weight of ethyl butyrate in fifteen minutes at 40° C. In view of the fact that clear solutions of lipase are less active than the unfiltered extracts from which they are prepared, it occurred to us to test the lipolytic activity of the residue after filtration. Accordingly, two 1-gram portions of the residue left, after filtering the above solution, were weighed out, and to one of these 100 cc. of distilled water were added, and to the other 100 cc. of a 0.2 per cent solution of sodium carbonate. These mixtures were then allowed to stand three days, at the end of which time they were filtered and their lipolytic activity tested in the usual manner. Tubes were prepared containing 10 cc. of the lipase solutions and 0.1 cc. of toluene. These were heated on the water-bath

for ten minutes at 40° C., and 0.26 cc. of ethyl butyrate was added to each tube. The tubes were then put back in the bath at 40° C. for fifteen minutes, at the end of which time they were placed in the ice-bath and titrated with N/20 caustic soda with the following results :

	N/20 caustic soda required. cc.	Percentage of hydrolysis.
Aqueous solution	0.51	1.28
0.2 per cent sodium carbonate solution	4.9	12.38

It is apparent from these results that the lipase contained in the residue left after precipitation with acid is comparatively insoluble in water, but is readily soluble in very dilute alkalies. The remarkable activity of the sodium carbonate extract as compared with the aqueous solution, together with the further fact that the alkaline solution also filters comparatively easily, led ultimately to the following methods for the preparation of clear solutions of lipase. Ten grams of fresh liver were thoroughly macerated with coarse white sand and made up to 500 cc. with water and 50 cc. of N/100 hydrochloric acid. The mixture was well shaken and allowed to stand over night. It was then filtered and the residue treated with 500 cc. of a 0.2 per cent solution of sodium carbonate. The activity of the two solutions was then tested in the usual manner : Temperature 40° C. ; quantity of ethyl butyrate used, equal to 0.26 cc., and 0.1 cc. of toluene as antiseptic ; time, fifteen minutes. The following results were obtained :

	N/20 NaOH required. cc.	Percentage of hydrolysis.
5 cc. acid solution of lipase, filtered	2.05	5.14
5 cc. of alkaline lipase, unfiltered	5.3	13.35

The sodium carbonate extract was then filtered and a clear reddish solution obtained. The lipolytic activity of this was tested at once, after which it was mixed with an equal volume of the hydrochloric acid solution described above, and the activity of the mixture was then tested, using 5 cc. of the

lipase solution, 0.26 cc. ethyl butyrate, 0.1 cc. of toluene, at 40° C. Time, fifteen minutes. The following results were obtained :

	N/20 NaOH required. cc.	Percentage of hydrolysis.
Acid solution of lipase	2.33	5.86
Alkaline solution of lipase	5.25	13.22
Mixed solution of lipase	4.3	10.83

These are the most active clear solutions of the lipolytic ferment that we have thus far been able to prepare. It has been found, however, that while very active, these clear solutions of lipase prepared by the use of sodium carbonate gave a heavy coagulum during the progress of hydrolysis, this being due, of course, to the coagulation of proteid matter by the butyric acid formed during the hydrolysis. Such, however, is not the case with the clear solutions of the ferment prepared by the use of very dilute acids, and hence the latter have been used altogether in our late work in studying the conduct of the enzyme toward ethyl butyrate.

It has also been found advantageous to employ butyric acid rather than hydrochloric in the preparation of clear solutions of the enzyme, the following method of preparation being finally adopted :

One gram of fresh hog liver is thoroughly macerated with powdered glass or coarse white sand and mixed with 75 cc. of water. The mixture is then heated to 35° C., and 5 cc. of N/10 butyric acid are added gradually and the mixture made up to 100 cc. with water. A heavy precipitate is formed which is filtered off by bringing the material on a folded filter. The filtrate, which has frequently been obtained without a vestige of color, is always perfectly clear and is usually slightly yellowish in tint. Five cc. of the clear extract prepared in this way has been found to hydrolyze from 5 to 6.25 per cent of ethyl butyrate in fifteen minutes at 40° C. when allowed to act on 0.26 cc. of the ethereal salt. In order to form some idea of the actual amount of lipase in the clear solutions prepared by means of N/10 butyric acid, 5 cc. of one

of these extracts were evaporated to dryness on the water-bath and dried in the air-oven at 110° C. to constant weight. The residue weighed 0.0047 gram ; in other words, these clear solutions cannot contain more than 5 milligrams of the ferment in 5 cc., and yet, as has already been pointed out above, this amount of the ferment can hydrolyze 0.0145 gram of ethyl butyrate, in fifteen minutes, under the general conditions employed in our experiments. In order to form some idea of the quantity of ethyl butyrate which this amount of lipase could hydrolyze in longer intervals the following experiment was tried : Five cc. of a clear solution of lipase which had been prepared on Dec. 30, 1902, were mixed with 0.26 cc. of ethyl butyrate and put in the incubator at 40° C. at 4 P. M., Dec. 30. After twenty-four hours, it required 10.3 cc. N/20 caustic soda to neutralize the butyric acid formed. It was then put back in the incubator at 40° C. for another twenty-four hours, at the end of which time it required 13.25 cc. N/20 caustic soda. A second portion of ethyl butyrate, 0.26 cc., was then added, when it was again placed in the incubator, where it remained until 10.30 A. M., Jan 4, 1903. It was found at this time to require 28.2 cc. N/20 caustic soda to neutralize the acid produced. Altogether, therefore, an amount of ethyl butyrate corresponding to 51.5 cc. N/20 caustic soda had been hydrolyzed in eighty-nine and a half hours ; hence an amount of lipase not exceeding 5 milligrams, and probably much less, had hydrolyzed nearly 300 milligrams of ethyl butyrate, or about sixty times its own weight of the ethereal salt, and yet at the end of this interval the ferment was practically as active as it was at the beginning of the experiment. Since the butyric acid produced considerably retards the hydrolysis, the quantity of ethyl butyrate hydrolyzed is certainly much less than that which would have been transformed had it been possible to remove the acid as fast as it was produced, or even if it had been neutralized as fast as formed. It should also be borne in mind that in all probability the 5 milligrams of total solids left on evaporating 5 cc. of the clear lipase solution did not consist entirely of the enzyme.

The Stability of Clear Solutions of Lipase.

It has been shown by Kastle and Loevenhart that, in perfectly dry condition, lipase is a stable substance. A mixture of fresh hog pancreas and sand, for example, that had been prepared and dried in the air on July 12, 1900, was found to be capable of hydrolyzing ethyl butyrate on Nov. 15, 1901. On the other hand, it was found that the ordinary aqueous extracts of the liver and pancreas soon lose their lipolytic power even when preserved under mild antiseptics, such as toluene and thymol. The clear solutions prepared by means of acids, however, have been found to be much more stable. Under the conditions ordinarily prevailing in the laboratory, they may be preserved for weeks and even months without exhibiting any marked falling off in lipolytic activity. This in itself is a great convenience, and seems to be due, in part at least, to the fact that small amounts of acid protect the solution of the ferment against putrefactive changes. Larger quantities of the acid, on the other hand, have been found to destroy the enzyme completely. Some idea of the stability of these clear solutions of the ferment and the preservative action of dilute acids may be obtained from an examination of the following data:

Five cc. of a 10 per cent liver extract were mixed with 19 cc. of water and 1 cc. of N/100 hydrochloric acid on October 21, 1902. The activity of the mixture was tested immediately and also after standing a certain interval, by allowing 5 cc. of it to act on 0.26 cc. ethyl butyrate for fifteen minutes at 40° C. The results of these measurements are as follows:

Date of test.	Amount of ethyl butyrate hydrolyzed. Gram.
Oct. 21, 1902	0.02552
" 27, 1902	0.02900
March 29, 1903	0.02378

It will be observed, therefore, that the solution had only lost 7 per cent of its lipolytic activity in five months. The increase in hydrolyzing power, observed after standing six days, is interesting, and is doubtless due to the liberation of

small amounts of lipase from its zymogen by the action of the dilute acid.   Similar results have been obtained in the case of other soluble ferments by other observers.   Similarly it has been found that clear solutions of the ferment prepared by precipitating its aqueous extracts with butyric acid are also quite stable, as may be seen from the following :

A clear solution of lipase was prepared on Jan. 28th by precipitating 100 cc. of a 1 per cent extract of liver in a 0.2 per cent solution of sodium carbonate with 15 cc. N/10 butyric acid, and filtering.   A small amount of thymol was added to the clear filtrate.   The activity of this solution was then tested immediately by allowing 5 cc. of it to act upon 0.26 cc. ethyl butyrate for fifteen minutes at 40° C.   Under these conditions 5 cc. of the clear solution were found to hydrolyze 7.25 per cent of the ethyl butyrate.   In order now to test the stability of this solution two tubes, each containing 5 cc. of the solution, were hermetically sealed and kept in a dark closet for eighty-three days at ordinary room temperature.   At the end of this time the tubes were opened and their lipolytic activity tested in the usual manner.   It was found that in one case 7.3 per cent of ethyl butyrate had been hydrolyzed in fifteen minutes at 40° C., whereas, in the second case, 7.25 per cent of the ethereal salt had been decomposed.   It is apparent, therefore, that this clear solution of lipase had suffered no diminution in activity during the eighty-three days that it had been kept in sealed tubes.   Similar results have been obtained with other clear solutions of lipase prepared by the action of acids on the aqueous extracts of the liver, indicating that very small amounts of acid exercise a preservative action on this enzyme.

On the Effect of Filtration through a Porous Cup on the Activity of Clear Solutions of Lipase.

It has been observed that the activity of clear solutions of lipase is not diminished even by repeated filtrations through ordinary filter-paper.   In studying the effect of various filtering media on the activity of solutions and extracts of the ferment, it has been found, however, that filtration through a

Pasteur-Chamberland filter completely removes the enzyme, even from its clear solutions. That such is the case may be seen from the following data :

A clear neutral solution of hepatic lipase was divided into two portions, one of which was filtered through a porous cup, while the other was preserved in its original condition. Both the filtered and unfiltered solutions were then tested towards ethyl butyrate in the usual manner, using 5 cc. of the extract and 0.26 cc. ethyl butyrate. Time, fifteen minutes; temperature, 40° C., with the following results :

	N/20 NaOH required. cc.	Amount of ethyl butyrate hydrolyzed. Gram.
Original solution	1.8	0.0104
Filtrate from porous cup	0.1	0.00058

In a second experiment, we obtained the following :

	N/20 NaOH required. cc.	Amount of ethyl butyrate hydrolyzed. Gram.
Original solution	1.6	0.00928
Fltrate	0.15	0.00087

It is apparent, therefore, that animal lipase belongs to the class of ferments that are retained by the walls of the porous cup.

The Kinetics of the Lipolytic Process.

In our earlier work on lipase, Loevenhart and one of us (Kastle) studied the effect of the concentration of the ethereal salt on the velocity of the hydrolysis, using ordinary aqueous extracts of the ferment. The coefficient of velocity was not observed to be constant, but showed a more or less regular falling off from the highest values obtained for short intervals of time. This retardation is doubtless to be explained by the fact that the acid liberated during the progress of the reaction exerts an inhibiting action on the ferment, and any other irregularities in our first values are doubtless to be explained by the more or less imperfect methods of investigation which were then employed, such as the use of an aqueous extract of the ferment, the constancy and homogeneity of which could not al-

ways be relied upon, and, secondly, the employment of larger amounts of ethereal salt than could be gotten into solution under the conditions of the experiment. It was determined, however, with reasonable exactness that for a given amount of the ferment the quantity of ethyl acetate and ethyl butyrate hydrolyzed in a given time was practically independent of the initial concentration of the ethereal salt.

Having obtained clear and uniform solutions of animal lipase, by the methods already described above, we were now in a better position to study the kinetics of the lipolytic process. In order, however, to make the necessary measurements, it was as essential to employ a solution of the ethereal salt, rather than a mixture thereof with water, as it was to make use of a solution of the ferment, rather than a turbid extract thereof. It was in this connection that the attempt was made originally to employ an alkali salt of one of the acid ethers, which as a class are characterized by great solubility in water. Unfortunately for our present purpose, it was found that lipase is unable to effect the hydrolysis of this class of substances. The results of this part of the investigation have already been published in this JOURNAL.[1] Such having proved to be the case, recourse was had to a dilute solution of ethyl butyrate, as the substance on which to make the necessary measurements. It was found that by vigorous shaking 1.2 cc. of pure ethyl butyrate, equal to 1.0931 grams, could be dissolved in a little less than 200 cc. of water. This very nearly represents the maximum solubility of this ester in water. The solution employed in our first measurements was prepared by vigorously agitating this amount of the ethereal salt with the required amount of water and making up the solution to a total volume of 200 cc. A solution containing 1 cc. of ethyl butyrate, 0.9109 gram, in a total volume of 200 cc., was also frequently employed. The strength of such solutions was determined by saponifying a known amount of the given solution with caustic soda, and also by completely hydrolyzing a known amount of it by means of lipase itself. The two methods not only gave numbers closely agreeing

[1] This JOURNAL, **27**, 481-486.

among themselves but also with the theory for the given amount of ethyl butyrate employed. This agreement was found to be so close, in fact, that in what follows the concentration of the solution of the ethereal salt is the calculated value for the particular solution employed. The clear solution of lipase employed in this part of the work was prepared by macerating 1 gram of fresh hog liver with coarse white sand. Seventy-five cc. of water were then added and the extract thus obtained was heated to 35° to 40° C. and precipitated with 5 cc. N/10 butyric acid. The solution was then made up to 100 cc. and filtered through a folded filter. A clear, golden-yellow solution of lipase was thus obtained. In many of our experiments this was employed directly, making the necessary correction for the initial acidity of the solution which was determined in every case. In many series of experiments, however, the clear lipase solution was first neutralized by means of standard caustic soda. In this manner all corrections for initial acidity of the extract were obviated. In our earlier work on lipase, Loevenhart and one of us (Kastle) found litmus to be by far the most satisfactory indicator. With the clear solution of the ferment, however, it by no means compares with phenolphthalein in point of delicacy, hence the latter has been used exclusively in this part of the work. With the view of determining the coefficient of velocity of the hydrolysis of ethyl butyrate by lipase, the following series of experiments were carried out, under slightly varying conditions, in the way of concentration, temperature, and time. Under each series of experiments will be found the exact conditions that obtained for that particular series.

Series I.

Conditions.—Fifty cc. ethyl butyrate solution, containing 1.0931 grams of ethyl butyrate in 200 cc., 50 cc. lipase, 5 cc. of which had an initial acidity equivalent to 0.45 cc. N/20 caustic soda. The solutions were mixed and allowed to stand for the several intervals indicated below at 21° C. At the end of each interval. 10 cc. of the mixture were removed from the flask by means of a pipette and titrated with N/20 caustic soda

deducting the initial acidity of the lipase from the amount required in each case. The value of the titer, in terms of the caustic soda employed, was found to be equivalent to 4.71 cc. for complete hydrolysis. This is the value of a^1 in the equation, $C = \frac{1}{t} \, ln. \, \frac{a}{a-x}$.

Time in minutes.	N/20 caustic soda required. cc.	C.
30	0.95	0.00751
64	1.45	0.00575
97	1.80	0.00496
132	2.25	0.00492
204	2.90	0.00469

Same as above except that the intervals were longer.

Time in minutes.	Caustic soda required. cc.	C.
60	1.30	0.00538
121	2.05	0.00472
198	2.75	0.00443
361	3.50	0.00376
467	3.80	0.00352

Series II.

Conditions.—Fifty cc. of ethyl butyrate solution were mixed with 25 cc. of neutral lipase solution and 25 cc. of water. The mixture was allowed to stand for the several intervals indicated below, at the end of which time 10 cc. of the mixture were removed by means of a pipette and titrated with N/20 caustic soda. Temperature $22°.5$ C., $a = 3.86$.

Time in minutes.	Caustic soda required. cc.	C.
15	0.45	0.00827
30.5	0.70	0.00656
48.5	1.00	0.00618
63.5	1.10	0.00528
78.5	1.25	0.00498
100.5	1.55	0.00519
133.5	1.80	0.00470
197.5	2.30	0.00467
266.0	2.70	0.00452

[1] In what follows the value of the whole titer, namely, a, is given for each series of experiments, in terms of the particular solution of sodium hydroxide employed in any given series of experiments. In this way the necessary correction has been made for any slight variation in the concentration of the sodium hydroxide, from the strength indicated in the tables.

Series III.

Conditions.—Twenty-five cc. ethyl butyrate solution were mixed with 10 cc. neutral lipase and 215 cc. of water. The mixture was allowed to stand for the required intervals at 22° C. Fifty cc. of the mixture were pipetted off at the end of each interval and titrated with N/50 caustic soda. In this series of experiments $a = 9.905$.

Time in minutes.	N/50 NaOH required. cc.	C.
15	0.53	0.00369
30	0.87	0.00307
46	1.15	0.00268
61	1.45	0.00259
76	1.75	0.00256

Series IV.

Conditions.—Twenty-five cc. ethyl butyrate solution were mixed with 10 cc. neutral lipase and 465 cc. of water, and the mixture allowed to stand for the desired intervals at 20° C. At the end of the several intervals, 50 cc. were removed by means of a pipette and titrated with N/100 caustic soda. In this series of experiments $a = 9.905$.

Time in minutes.	N/100 NaOH required. cc.	C.
16	0.65	0.00424
31	0.90	0.00307
46	1.35	0.00318
61	1.45	0.00259
91	1.98	0.00244
121	2.35	0.00224
151	2.75	0.00215
181	3.25	0.00219

In this connection we desire to call attention to the results of the several series of observations given under the head of the effect of temperature on the velocity of the hydrolysis (p. 540). In general, the results therein enumerated are altogether similar to those given in Series 1 to 4, inclusive. In this connection, however, it will be observed, under the head of the effect of temperature on the velocity of the reaction, that in Series 3 at 20° C. and in Series 5 at 40° C.

much more constant values for the coefficient of velocity have been obtained. In fact, in these two series of experiments the several values of C as calculated from the equation

$$C = \frac{1}{t} \, ln. \, \frac{a}{a - x},$$

are sufficiently concordant to indicate that the reaction under consideration is monomolecular. Taken collectively, however, it will be observed that the several values of C for any particular series show a slight, or sometimes considerable, falling off from the first value thereof, indicating a somewhat higher initial rate of hydrolysis than that which obtains for subsequent intervals. It seemed probable that this gradual retardation of the hydrolysis was brought about by the inhibiting action of the acid produced during the hydrolysis. That such is the case is apparent from the following experiments :

In order to determine the effect of free butyric acid on the progress of the hydrolysis, two experiments were tried. A mixture, No. 1, was made, containing 5 cc. of neutral lipase, 10 cc. of ethyl butyrate, and 35 cc. of water, and a second, No. 2, was prepared containing 5 cc. of neutral lipase, 10 cc. of ethyl butyrate, 3 cc. of N/50 butyric acid, and 32 cc. of water. These solutions, Nos. 1 and 2, were allowed to stand at 22° C. for the several intervals indicated below, at the end of which the entire solutions were titrated with N/50 caustic soda, making allowance, of course, for the caustic soda used in neutralizing the free butyric acid in Experiment 2, at the end of the first interval. The several amounts of caustic soda required, together with the several values of C calculated for each interval separately, are given below. $a = 19.81$.

Experiment 1.

Time in minutes.	N/50 caustic soda required. cc.	C.
15	1.6	0.00561
15	1.15	0.00433
15	1.1	0.00443

Experiment 2.

Time in minutes.	N/50 caustic soda required. cc.	C.
15	1.125	0.00390
15	1.15	0.00422
15	1.1	0.00431

Similar experiments were tried with N/50 hydrochloric acid. Two experiments were set up : No. 1 contained 5 cc. neutral lipase, 10 cc. ethyl butyrate, and 35 cc. water. No. 2 contained 5 cc. neutral lipase, 10 cc. ethyl butyrate, 3 cc. N/50 hydrochloric acid, and 32 cc. water. These were allowed to stand for the several intervals indicated below at a temperature of 25° C., and the whole solution was titrated at the end of each interval, due allowance being made for the caustic soda required by the N/50 hydrochloric acid originally present in No. 2. $a = 19.81$.

Experiment 1.

Time in minutes.	N/50 caustic soda required. cc.	C.
15	1.55	0.00543
15	1.35	0.00512
15	1.30	0.00533

Experiment 2.

Time in minutes.	N/50 caustic soda required. cc.	C.
15	0.65	0.00223
15	1.4	0.00505
15	1.3	0.00507

The following are the results of another series of experiments showing the effect of N/50 hydrochloric acid on the rate of hydrolysis of ethyl butyrate by lipase :

Experiment 1.

Conditions.—Five cc. neutral lipase, 10 cc. ethyl butyrate, 35 cc. water. Temperature 22° C. $a = 19.81$.

Time in minutes.	N/50 caustic soda required. cc.	C.
15	1.4	0.00489
15	0.95	0.00352
15	1.05	0.00412

Experiment 2.

Conditions.—The same as those given under Experiment No. 1, except that 3 cc. of N/50 hydrochloric acid and 32 cc. of water were employed instead of 35 cc. of water, $a = 19.81$.

Time in minutes.	N/50 caustic soda required. cc.	C.
15	0.6	0.00205
15	1.00	0.00357
15	1.10	0.00417

It is evident from these results that the presence of free acid, either hydrochloric or butyric, greatly diminishes the velocity of the reaction during the first interval. It is interesting to note, however, that the several coefficients of velocity obtained for the successive intervals are practically the same in all cases, indicating that the effect of these small quantities of free acid on the ferment is purely a temporary one. In general it may be said that small amounts of free acid greatly inhibit the action of the enzyme but do not permanently destroy its activity. On the other hand, we have observed in other experiments that larger amounts of acids completely destroy the ferment.

Determination of the Order of the Lipolytic Reaction by van't Hoff's Method.

In order to determine the precise nature of the change here under consideration we have made use of van't Hoff's method, which depends upon the effect of change of concentration on the velocity of the reaction. This was carried out in the following manner : 10 cc. of neutral lipase were mixed with 25 cc. of ethyl butyrate and 15 cc. of water. The total of 50 cc. represents the unit of volume. This was allowed to stand for thirty minutes at 20° C. Ten cc. of the mixture were then removed by means of a pipette and the free acid determined by means of N/100 caustic soda. It required 1.3 cc. of N/100 caustic soda. Simultaneously with the removal of the 10 cc. employed in the titration, the remainder of the original solution, 40 cc., was made up to a total volume of 90 cc. with water and kept for another interval of thirty minutes under exactly

the same conditions of temperature, etc., as before. At the end of this time, 20 cc. of the second mixture were drawn out by means of a pipette and the free acid determined, which required 2.25 cc. N/100 caustic soda. The ethyl butyrate solution employed was of such strength that if all of the 25 cc. originally used in the experiment had been hydrolyzed, the free acid produced would have required 99.05 cc. of the N/100 caustic soda employed. Representing by this number the original concentration, the concentration at the end of the first thirty minutes may be represented by 92.55, since 99.05 — (1.3 × 5) = 92.55. We may therefore tabulate these results as follows :

Time in minutes.	Concentration.
0	99.05
30	92.55

Mean concentration, 95.8

If now 92.55 cc. of N/100 caustic soda is the equivalent of 50 cc. of the mixture at the end of the first thirty minutes, the 40 cc. of the mixture remaining which had been diluted up to 90 cc. with water, contained an amount of ethyl butyrate equivalent to four-fifths of 92.55 cc. of N/100 caustic soda, namely, 74.04. If this amount was present in 90 cc., then 50 cc. of this, which was taken as the unit volume, contained at that time an amount of ethyl butyrate equivalent to five-ninths of 74.04, namely, 41.13. This last number, therefore, represents the concentration at the beginning of the second interval, and since 20 cc. of the mixture contained free acid equivalent to 2.25 cc. N/100 caustic soda, the total amount of acid present was equivalent to 10.125 N/100 caustic soda. Subtracting from this the amount of acid present at the beginning of the second interval, namely, 1.3 × 4 = 5.2, we get 4.925 cc. N/100 caustic soda as the equivalent of the total acid produced during the second interval, and in 50 cc. of this, the unit volume, there was produced during that time an amount of acid equivalent to five-ninths of 4.925 or very nearly 2.73 cc. N/100 caustic soda. Subtracting this from 41.13 we obtain the concentration at the end of the second interval,

namely, 38.40. Hence we have the following data for the
second interval :

Time in minutes.	Concentration.
0	41.13
30	38.40

Mean concentration for the second interval, 39.765

Substituting these several values in van't Hoff's equation,
we arrive at the number representing the order of the reac-
tion under consideration :

$$n = \frac{\log \left\{ \frac{dC_1}{dt} : \frac{dC_2}{dt} \right\}}{\log (C_1 : C_2)} = \frac{\log \frac{dC_1}{dt} - \log \frac{dC_2}{dt}}{\log C_1 - \log C_2}.$$

$$\frac{dC_1}{dt} = \frac{99.05 - 92.55}{30} = \frac{6.5}{30} = 0.21667 ; \ C_1 = 95.8.$$

$$\frac{dC_2}{dt} = \frac{41.13 - 38.40}{30} = \frac{2.73}{30} = 0.091 ; \ C_2 = 39.765.$$

$$\log_e 0.21667 = -1.5294 ; \ \log_e 0.091 = -2.3969.$$

$$\log_e 95.8 = 4.5623 ; \ \log_e 39.765 = 3.6830.$$

$$\therefore \ n = \frac{-1.5294 - (-2.3969)}{4.5623 - 3.6830} = \frac{0.8675}{0.8793} = 0.986.$$

A second determination of N from other data gave 0.974.

There can be no doubt, therefore, that in the hydrolysis of
ethyl butyrate by lipase we have to deal with a monomolecu-
lar process, which is influenced to a slight extent by one of
the products of the change, namely, the acid. It has also
been found that alcohol slightly retards the action of the fer-
ment, but with the small quantities of this substance resulting
from the hydrolysis of dilute solutions of the ethereal salt its
effect is so slight as to be altogether negligible.

On the Effect of Temperature on the Rate of Hydrolysis of Ethyl Butyrate by Lipase.

In his " Études de Dynamique Chimique " van't Hoff[1] has

[1] " Études de Dynamique," van't Hoff's English Translation, 1896, page 125.

pointed out that in the greater number of cases thus far inves-
tigated, the ratio of the velocity constants of a chemical reac-
tion for two temperatures differing by 10° C. has a value be-
tween 2 and 3 approximately. In other words, a rise of tem-
perature of 10° C. doubles or sometimes trebles the velocity of
a reaction. Among other examples, he cites the following :

Reaction.	Mean ratio of velocities at T and (T + 10).
Hydrolysis of ethyl acetate	1.89 and 2.03
" " acetamide	2.12
Inversion of cane-sugar	3.63
Hydrolysis of tertiary amyl acetate	2.19

It therefore occurred to us that it would be interesting to
determine the velocity constants of the reaction under investi-
gation, at several temperatures differing from one another by
10° C. Accordingly the rate of hydrolysis has been determined
at 0° C., 10° C., 20° C., 30° C., and 40° C. The results of
these measurements, together with all necessary data, are
given in the following tables :

Series 1.

Quantities of Substances Employed. — Temperature 0° C.

> 10 cc. neutral lipase
> 25 cc. ethyl butyrate
> 15 cc. water
> 50 cc. total volume
> Amount titrated at end
> of each interval, 10 cc.
> $a = 19.81$

Time in minutes.	N/100 caustic soda required. cc.	C.
15	0.20	0.00068
30	0.45	0.00077
45	0.70	0.00080
60	0.80	0.00069
75	0.90	0.00062
	Average,	0.000712

Series 2.

Quantities of Substances Employed.—Same as in Series 1. Temperature 10° C.

Time in minutes.	N/100 caustic soda required. cc.	C.
15	0.45	0.00153
30	0.75	0.00129
45	1.05	0.00121
60	1.30	0.00113
75	1.60	0.00112

Average, 0.001256

Series 3.

Quantities of Substances Employed.—Same as in Series 1. Temperature 20° C.

Time in minutes.	N/100 caustic soda required. cc.	C.
15	0.65	0.00223
30	1.35	0.00235
45	1.80	0.00212
60	2.2	0.00206
75	2.95	0.00215

Average, 0.00218

Series 4.

Quantities of Substances Employed.—Same as in Series 1. Temperature 30° C.

Time in minutes.	N/100 caustic soda required. cc.	C.
15	1.15	0.00399
30	2.15	0.00383
45	3.10	0.00378
60	3.85	0.00360
75	4.60	0.00352

Average, 0.00374

Series 5.

Quantities of Substances Employed.—Same as in Series 1. Temperature 40° C.

Time in minutes.	N/100 caustic soda required. cc.	C.
15	1.65	0.00580
30	3.15	0.00577
45	4.55	0.00580
60	5.75	0.00571
75	7.15	0.00597
	Average,	0.00581

From these results the following mean ratio of velocities for the reaction at the several intervals of temperature have been calculated. These are as follows :

Series compared.	Ratio of velocities at T and (T + 10).
1 and 2	1.76
2 and 3	1.74
3 and 4	1.71
4 and 5	1.55
Average,	1.69

The Catalytic Power of Lipase.

It has already been pointed out above that lipase can hydrolyze three times its weight of ethyl butyrate in fifteen minutes, or about sixty times its weight in eighty-nine and a half hours, when allowed to act upon an excess of the ethereal salt, under the conditions usually employed in the earlier part of our work on the ferment. A much better idea of the action of lipase as a catalyzing agent, however, can be gained from the following experiment: 10 cc. of neutral lipase were mixed with 10 cc. of ethyl butyrate solution. This mixture was allowed to stand at 22° C. for a certain interval and then titrated with N/20 sodium hydroxide, using the whole of the mixture as the titer. After neutralization the mixture was set aside and at the end of a second interval, its acidity was determined in the same way. The following are the results of the several titrations for the several intervals, using the whole of the solution in each titration. In calculating the several values of C., we have ignored the change in concentration of the original solution, due to the addition of the successive portions of caustic soda. This is permissible since

it has been shown that the amount of ethyl butyrate hydro-lyzed is largely independent of the amount of water in which it is dissolved.

No. of intervals.	Total time in minutes.	N/20 sodium hydroxide required at end of each interval. cc.	Total volume N/20 NaOH required for given time. cc.	C. ($a = 7.71.$)
I	15	1.4	1.4	0.01336
2	32	1.5	2.9	0.01474
3	45	1.2	4.1	0.01686
4	60	1.3	5.4	0.02009
5	76	1.2	6.6	0.02550
6	91	0.8	7.4	0.03531
7	106	0.3	7.7	. . . . . .
8	120	0.15	7.85	. . . . . .

Average,   0.02094

It will be observed that at the end of an interval of one hundred and twenty minutes all of the ethyl butyrate had been decomposed. In order, therefore, to determine whether the lipase in this solution had suffered any diminution in activity a second portion of ethyl butyrate solution, namely 10 cc., was added and the whole mixture titrated with N/20 sodium hydroxide at the end of certain intervals as before. The following are the results of the second series of titrations :

No. of intervals.	Total time in minutes.	N/20 sodium hydroxide required at end of each interval. cc.	Total volume N/20 NaOH required for given time. cc.	C. ($a = 7.71.$)
I	15	1.56	1.55	0.01496
2	32	1.65	3.20	0.01676
3	37	1.40	4.60	0.01932
4	62	1.25	5.85	0.01393
5	78	1.05	6.90	0.02889
6	99	0.60	7.50	0.03639
7	120	0.30	7.80	. . . . . .

Average,   0.02321

We see, therefore, that at the end of the second series of measurements, namely, during an interval of one hundred and twenty minutes, just as much ethyl butyrate was hydrolyzed as during the first period of one hundred and twenty minutes. It would seem, therefore, that lipase suffers no permanent alteration while effecting the hydrolysis of the ethereal salt, but that it retains its complete activity regardless of the amount of substance that it has previously hydrolyzed. In this sense it belongs to the class of true catalyzing agents. The increase in the value of C in these two series of experiments and the slight increase of the values of C in the second series as compared with the first is probably due to the fact that lipase acts more rapidly in a neutral or slightly alkaline medium than in an acid one.

On the Influence of Concentration of the Ethyl Butyrate on Its Hydrolysis by Lipase.

Some of our earlier experiments seemed to indicate that the amount of ethyl butyrate hydrolyzed by lipase is within certain limits independent of the concentration of the ethereal salt. That such is the case may be seen from the following :

A series of six experiments was set up, using 5 cc. of a clear lipase solution and 5 cc. of a solution of ethyl butyrate (1.2 cc. of the compound in 200 cc.) in each experiment. The concentration was varied by the addition of the several amounts of water indicated below. The lipase was allowed to act for twenty hours at 18° C in each experiment.

No. of experiment.	Volume of water used. cc.	Concentration of ethyl butyrate per liter.	Volume N/20 sodium hydroxide required. cc.	Percentage of ethyl butyrate hydrolyzed.
1	0	2.7328	3.40	72.18
2	10	1.3664	3.60	76.43
3	20	0.9109	3.50	74.31
4	30	0.6832	3.65	77.49
5	40	0.5466	3.65	77.49
6	50	0.4554	3.70	78.55

In a second series of experiments,[1] 1 cc. of a dilute solution of clear lipase and amounts of ethyl butyrate solution, varying from 1 cc. to 8 cc. were employed. The whole was then made up to a total volume of 10 cc. in each case, and the several mixtures kept at 40° C. for six hours, at the end of which time they were titrated with N/20 sodium hydroxide, with the following results:

No. of experiment.	Amount of ethyl butyrate in 10 cc. Gram.	Vl'me N/20 sodium hydroxide required. cc.	Amount of ethyl butyrate hydrolyzed. Gram.	Perc'nt'ge of ethyl butyrate hydrolyzed.
1	0.0055	0.80	0.0046	83.6
2	0.0110	1.55	0.0090	81.8
3	0.0175	2.40	0.0140	80.1
4	0.0220	3.10	0.0180	80 1
5	0.0275	3.60	0.0210	76.0
6	0.0330	4.35	0.0254	77.0
7	0.0385	4.85	0.0283	73.6
8	0.0440	5.00	0.0292	66.3

In a third series of experiments designed to show the effect of concentration on the hydrolysis of the ethyl butyrate by lipase, 0.05 gram of the fresh liver tissue was employed in each experiment, together with 10 cc. of ethyl butyrate solution (1.2 cc. in 200 cc.), and at a total dilution of 10, 20, and 30 cc. The flasks containing these mixtures were kept at 21° C. for forty minutes, at the end of which time they were titrated with N/20 sodium hydroxide, with the following results:

[1] The results of this series of experiments would seem at first glance to indicate that the hydrolysis is directly proportional to the amount or ethyl butyrate present, may be seen, for example, by comparing Experiments 1, 2, and 3; but a more careful comparison of all of these results will show that this is true only in the case of very small amounts of the ethereal salt, as may be seen from a comparison of Experiments 1 and 8. This explains, therefore, why it is possible under certain conditions to increase the quantity of ethereal salt without causing any noticeable increase in the hydrolysis, as may be seen from Series 1, 2, 3, and 4 under this head.

No. of experiment.	Dilution.	Amount of ethyl butyrate present. Gram.	N/20 sodium hydroxide required. cc.	Amount of ethyl butyrate hydrolyzed. Gram.	Perc'nt'ge of ethyl butyrate hydrolyzed.
1	10	0.0550	1.8	0.0105	19.1
2	20	"	1.7	0.00993	18.5
3	30	"	2.3	0.0134	24.18

After the first titration the flasks were set aside and allowed to stand for three hours and forty-five minutes, at the end of which time they were titrated again with the following results :

No. of experiment.	N/20 sodium hydroxide required at end of second interval. cc.	Amount of ethyl butyrate hydrolyzed during second interval. Gram.	Percentage of ethyl butyrate hydrolyzed during second interval.
1	4.15	0.0242	44.00
2	3.90	0.0228	41.45
3	4.05	0.0237	43.09

With the view of throwing still further light on this point, four series of experiments were carried out with the following amounts of substances, under the following conditions :

1. Contained 5 cc. neutral lipase, 10 cc. ethyl butyrate solution (1 cc. in 200 cc.) and 10 cc. of water.

2. Five cc. of neutral lipase and 20 cc. of ethyl butyrate solution.

3. Five cc. of neutral lipase, 10 cc. of ethyl butyrate solution, and 40 cc. of water.

4. Five cc. of neutral lipase and 50 cc. ethyl butyrate solution.

These several solutions were allowed to stand at 19° C. At the end of fifteen-minute intervals, the whole of each solution was titrated with N/50 sodium hydroxide, with the following results :

Series 1.

$$a = 19.81.$$

No. of intervals.	Time in minutes.	N/50 sodium hydroxide required. cc.	C.
1	15	1.55	0.00543
2	30	2.75	0.00498
3	45	3.90	0.00487
4	60	5.05	0.00490
5	75	6.20	0.00501
6	90	7.30	0.00511
7	105	8.30	0.00517

Average C_1, 0.00507

Series 2.

$$a = 2 \times 19.81.$$

No. of intervals.	Time in minutes.	N/50 sodium hydroxide required. cc.	C.
1	15	1.65	0.00283
2	30	2.95	0.00259
3	45	4.20	0.00249
4	60	5.35	0.00242
5	75	6.55	0.00241
6	90	7.80	0.00244
7	105	8.95	0.00244

Average C_1, 0.00252

Series 3.

$$a = 19.81.$$

No. of intervals.	Time in minutes.	N/50 sodium hydroxide required. cc.	C.
1	15	1.80	0.00635
2	30	3.05	0.00557
3	45	4.30	0.00544
4	60	5.60	0.00554
5	75	6.85	0.00566
6	90	8.00	0.00575
7	105	9.20	0.00594

Average C_1, 0.00575

Series 4.

$$a = 5 \times 19.81.$$

No. of intervals.	Time in minutes.	N/50 sodium hydroxide required. cc.	C.
I	15	2.00	0.00135
2	30	3.45	0.00118
3	45	4.80	0.00110
4	60	6.15	0.00107
5	75	7.50	0.00105
6	90	8.85	0.00104
7	105	10.20	0.00103

Average C_1, 0.00112

If now we compare the velocity constants, C, for the first interval of the several series and the average velocity constants C_1 for the several series we obtain the following :

Velocity Constants for the First Interval.

		c.
Series 1		0.00543
" 2	0.00283×2	0.00566
" 3		0.00635
" 4	0.00135×5	0.00675

Average Velocity Constants.

		c_1.
Series 1		0.00507
" 2	0.00252×2	0.00504
" 3		0.00575
" 4	0.00112×5	0.00560

We see, therefore, that the general trend of these results indicates that the amount of the ethyl butyrate hydrolyzed by lipase is, within certain limits, independent of the concentration of the ethereal salt, thereby confirming our earlier results on this phase of the problem. The fact that the rate of hydrolysis is slightly higher the more dilute the solution of ethyl butyrate, and that somewhat larger amounts of the ester are hydrolyzed in the more dilute solutions is doubtless to be explained by the fact that in the more concentrated solutions the acid resulting from the hydrolysis reaches a greater con-

centration than in the more dilute solutions, and hence exercises a greater inhibiting action on the ferment.

The Comparative Activity of Lipase, Hydrochloric Acid, and Sodium Hydroxide towards Ethyl Butyrate.

So little is known as to the real nature of the hydrolyzing enzymes, that it seemed to us of interest to compare lipase with dilute hydrochloric acid and caustic soda, as to their power to hydrolyze ethyl butyrate, since all three of these substances can effect the decomposition of ethereal salts. A clear solution of lipase was employed, 5 cc. of which gave, on evaporation and drying in the air at 110° C., 0.0047 gram solid residue. As already pointed out above, it is not at all probable that all of this solid residue consists entirely of the ferment. On the other hand, considering the great variety of substances present in the liver, it seems more than likely that only a small amount of this residue consists of the lipolytic ferment. For the purpose of comparison, however, it was considered advisable to regard it as consisting of pure lipase, and to compare it therefore with about an equal quantity of hydrochloric acid and caustic soda, in estimating their respective hydrolyzing powers.

Accordingly three experiments were arranged as follows :

1. Twenty-five cc. of a clear solution of lipase were neutralized with dilute sodium hydroxide and made up to 50 cc. To this, 25 cc. of ethyl butyrate solution were then added and the mixture allowed to stand at 20° C. for the desired time. At the end of certain intervals 10 cc. of the mixture were withdrawn by means of a pipette and titrated with N/100 sodium hydroxide. The results obtained were as follows :

Time in minutes.	N/100 sodium hydroxide required. cc.	Percentage of ethyl butyrate hydrolyzed.
0	0.0	0.0
85	5.8	6.92
155	8.3	9.90
1218	11.8	14.07

2. Five cc. N/10 sodium hydroxide were mixed with 45 cc. of water and 25 cc. of ethyl butyrate solution. This mixture

was then allowed to stand at 20° C., and at certain intervals 10 cc. of it were withdrawn by means of a pipette and a quantity of hydrochloric acid added equivalent to the amount of caustic soda originally present. The excess of acid, corresponding to the amount of ethyl butyrate saponified in the given time, was then titrated with N/100 sodium hydroxide. The results of these measurements are as follows :

Time in minutes.	N/100 Sodium hydroxide required. cc.	Percentage of ethyl butyrate decomposed.
0	0.0	0.0
86	5.11	5.22
158	5.91	5.33
164	6.06	6.19
1220	6.31	6.44

3. Five cc. N/10 hydrochloric acid were brought together with 45 cc. of water and 25 cc. of ethyl butyrate solution, and allowed to stand at 20° C. for a certain time. At intervals, 10 cc. of the mixture were withdrawn and titrated with N/100 sodium hydroxide. After making allowance for the initial acidity, the following results were obtained :

Time in minutes.	N/100 Sodium hydroxide required. cc.	Percentage of ethyl butyrate hydrolyzed.
0	0.0	0.0
86	0.0	0.0
167	0.0	0.0
1224	0.2	0.204

It is evident from these results that lipase probably far exceeds both caustic soda and hydrochloric acid in its power to hydrolyze ethyl butyrate in dilute solution. It is further evident that it cannot partake of the nature of an acid, since even one of the strongest acids known, namely, hydrochloric, is far removed from it in its power to hydrolyze ethyl butyrate. On the other hand, it would seem reasonable to conclude that if this ferment has any analogue at all among ordinary chemical compounds, it more nearly resembles sodium hydroxide than it does hydrochloric acid, at least, in so far as its action on ethyl butyrate is concerned. In this connection it is interesting to note that Hanriot has reached similar conclusions

respecting the chemical nature of lipase from altogether differ-ent premises. According to this observer, the basic nature of lipase would not only explain its power to hydrolyze ethereal salts but would also enable us to understand the inhibiting and destructive action of acids on the activity of the ferment.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, KENTUCKY,
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AMMONIUM SULPHOCYANATE AND THIOUREA AS SOURCES OF NITROGEN TO FUNGI AND MICRO-ORGANISMS.

BY JOSEPH H. KASTLE AND ELIAS ELVOVE.[1]

It occurred to one of us, Kastle, that it might prove of in-terest to determine to what extent the nitrogen of ammonium sulphocyanate and thiourea is available for the life and growth of fungi and micro-organisms, and also to what extent we could discriminate between these isomers by biochemical methods.

In this connection it may be observed in passing that the sulphocyanates and thiourea suffer no change in the animal organism. That such is the case we must conclude from the work of Pollak[2] and from certain unpublished results obtained by Kastle in 1902. The former found that sodium sulphocyan-ate, when administered by the mouth, and subcutaneously to man and the lower animals, could be practically all re-covered from the urine unchanged, and also that the "surviv-ing liver" had no power of decomposing the sulphocyanates. The following experiments were carried out by Kastle : 0.5 gram of ammonium sulphocyanate in a small amount of water was injected subcutaneously into a guinea pig. For some time no effects were observable. In about an hour, however, the animal became restless and convulsions soon set in, which were much intensified by any sudden noise or irritation. The animal died in two and a half hours after the injection, in all probability from ammonium poisoning. The post-mortem examination showed some fatty degeneration of the liver, and

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[1] Research Assistant in the Carnegie Institution of Washington.

[2] Beitr. chem. phys. Path., **2**, 430–433 (1902).

the intestines were greatly distended with gas. The bladder was empty and no urine was passed during the experiment. The blood and several of the tissues and organs gave abundant tests for sulphocyanate, indicating that this compound is not converted into thiourea in the organism ; in fact, there was nothing to indicate that it had been changed in any way.

To a second pig, 0.5 gram of thiourea was administered subcutaneously. At first this pig exhibited greater distress than did the one which received the ammonium sulphocyanate. At the end of an hour, it was observed to be in a somewhat listless, semi-comatose condition. It completely recovered over night, however, and remained healthy and active until the conclusion of the experiment. During the progress of the experiment it passed urine freely. This was collected twenty-four and forty-eight hours after the injection, and on both occasions was found to contain an abundance of thiourea, but no sulphocyanate. From these results, together with those of Pollak, it would seem that both of the compounds remain unaltered in the animal organism.

Such being the case, it occurred to us to study the growth of certain fungi and micro-organisms in nutritive solutions containing these two substances as nitrogenous food material. Accordingly a nutritive solution was prepared, containing 25 grams of cane-sugar, 0.25 gram calcium phosphate, 0.2 gram potassium carbonate, 0.2 gram magnesium carbonate, and 0.2 gram potassium phosphate in 500 cc. of distilled water. To 200 cc. of this solution 0.5 gram of ammonium sulphocyanate was added, and to a second portion of 200 cc. of the original solution 0.5 gram of thiourea was added. These solutions were labeled I. and II. respectively. Six tubes were then prepared containing about 5 cc. each of solution I. and similarly a series of tubes with solution II. These tubes were then sterilized and inoculated with a pure culture of green mold, *Penicillium glaucum*, on November 4th, after which they were put away in a dark closet at room temperature, and examined from time to time for growth of the mold with the following results :

Time.	I.	II.
5 days	Three of the tubes showed vigorous growth of mold. Fructification in one tube.	No distinct growth in any of the tubes.
10 days	Plentiful growth in all tubes. Fructification in one tube.	Very uncertain and sparing growth in one tube.
15 days	Vigorous growth with fructification in all tubes.	Sparing growth of mycelium in two out of six tubes.

It is evident from these results that at least a part of the nitrogen of ammonium sulphocyanate is available or the growth of the green mold, whereas that of thiourea cannot support the growth of this fungus. In order to determine whether the thiourea was really poisonous to the spores of the mold, or whether it simply could not furnish the nitrogen essential to the plant, portions of solution I., containing ammonium sulphocyanate, were inoculated with some of the material that had remained in contact with solution II., containing the thiourea, for fifteen days. After three days, growth had started in all except one of the tubes thus prepared, and after fourteen days there was growth in all of the tubes of this series, indicating that while the thiourea is not poisonous to the fungus, its nitrogen is unavailable for its growth. It further appears that only the ammonium nitrogen of ammonium sulphocyanate is available for the needs of the plant. That such is the case may be gathered from the following experiments with potassium sulphocyanate.

A solution similar to solution I. was prepared, except that it contained 0.5 gram of potassium sulphocyanate instead of ammonium sulphocyanate. Six tubes containing this solution were inoculated with spores of *Penicillium glaucum*. At the end of fourteen days no growth of the mold was to be observed in any of these tubes; 0.05 gram of ammonium tartrate was then added to each tube, after which they were allowed to stand for a further interval. Ten days after the addition of the ammonium tartrate an abundant growth with fructification was observed in four out of the six tubes. It would seem, there-

fore, that while the sulphocyanate ion is not poisonous to the fungus, the nitrogen thereof is not available for its growth.

Similar results have been obtained with yeast. A nutrient solution, A, was prepared, containing the following substances :

Potassium phosphate	1.0 gram
Calcium phosphate	0.1 "
Magnesium sulphate	0.1 "
Cane-sugar	75.0 grams.
Water	500 cc.

To 100 cc. of this solution 0.5 gram of ammonium tartrate was added ; to a second portion of 100 cc. of the solution 0.5 gram ammonium sulphocyanate was added, and to a third portion of the solution, 100 cc., there was added 0.5 gram of thiourea. The three solutions were then sterilized and inoculated with a culture of pure yeast, after which they were put in the incubator and kept at 30° C. for several days. At the end of three days, the flasks containing the ammonium tartrate and sulphocyanate showed an abundant growth of yeast, whereas the flask containing the thiourea showed none, or at most a mere trace. The flasks containing the ammonium tartrate and sulphocyanate both developed a strong alcoholic odor, whereas the flask containing the thiourea gave no evidence of alcoholic fermentation.

On the other hand, it is interesting to note in this connection, that while thiourea is unable to supply the nitrogen necessary for the growth and reproduction of the yeast, it does not prevent alcoholic fermentation, provided a sufficient amount of yeast is present originally in the saccharine liquid. That such is the case may be seen from the following experiments :

Three flasks were prepared, each containing 50 cc. of nutritive solution A. To one of these 0.1 gram of ammonium tartrate was added, to the second 0.1 gram of ammonium sulphocyanate, and to the third 0.1 gram of thiourea. 0.1 gram of yeast was then added to each flask. On standing over night at 30° C., all three flasks showed alcoholic fermentation. This

experiment was repeated, using glucose instead of cane-sugar, with essentially the same results.

The difference between ammonium sulphocyanate and thiourea, so far as the availability of nitrogen is concerned, has also been demonstrated by means of the various micro-organisms of putrid cheese. A nutrient solution was prepared, containing the following substances :

Calcium phosphate	0.25 gram
Potassium phosphate	0.20 "
Potassium carbonate	0.20 "
Magnesium sulphate	0.20 "
Cane-sugar	25.00 grams
Water	500 cc.

This solution was divided into five equal portions: To (1) nothing was added ; to (2) 0.1 gram ammonium chloride ; to (3) 0.1 gram potassium nitrate ; to (4) 0.1 gram ammonium sulphocyanate; and to (5) 0.1 gram thiourea. These solutions were placed in flasks and sterilized, after which they were inoculated with putrid cheese. The flasks were then placed in the incubator and kept at 30° to 35° C. At the end of one week flasks (2) and (4) showed an abundant growth of micro-organisms, whereas no bacterial growth was observed in the other three. At the end of three weeks the flask containing the ammonium sulphocyanate showed the most abundant growth of any of the flasks, being literally filled with mold and other organisms. The flask containing the ammonium chloride also contained an abundant growth. The flask containing the thiourea showed only very slight growth, as did the flasks containing the potassium nitrate and no other nitrogen compound.

Conduct of Ammonium Sulphocyanate and Thiourea towards the Nitrifying Organisms of the Soil.

In view of the fact that the nitrogen of ammonium sulphocyanate is available to certain fungi and micro-organisms, whereas that of thiourea is not, it occurred to us that these two compounds might conduct themselves differently to the

nitrous and nitric organisms of the soil with respect to the formation of nitrite and nitrate.[1]

With the view, therefore, of testing the conduct of these two isomers towards the nitrifying organisms of the soil the following experiments were carried out :

Four solutions were prepared : No. 1 contained 0.1 gram of ammonium chloride, 0.002 gram of magnesium sulphate, 0.004 gram of potassium phosphate, an excess (0.5 gram) of calcium carbonate, in 100 cc. of water.

No. 2 differed from No. 1 only in that it contained 0.1 gram urea in place of the ammonium chloride.

No. 3. Same as No. 1 except that it contained 0.1 gram ammonium sulphocyanate instead of ammonium chloride.

No. 4. Same as No. 1 except that it contained 0.1 gram thiourea in place of ammonium chloride.

To each of the solutions 0.1 gram of pasture soil was added, and small portions of the several mixtures tested at once for nitrates and nitrites with diphenylamine and Griess' sulphanilic acid reagent. None of the solutions gave the slightest test with either of the reagents. The flasks containing the several mixtures were then closed with a plug of cotton wool and kept in the dark, at room temperature, for a number of days. They were then tested from time to time with diphenylamine with the following results :

	Color with diphenylamine.			
Time.	1.	2.	3.	4.
19 hours	Light blue	None	None	None
41 "	Blue	Light blue	"	"
89 "	Dark blue	" "	Faint blue	"

At the end of fifteen days the quantity of nitrite in each of the solutions was determined colorimetrically with the sulphanilic acid reagent, with the following results :

Solution.	Milligrams N_2O_3.
1	1.2
2	0.40
3	0.03
4	None

[1] Since this communication was written we have come across an observation by Munro, bearing on this subject. This observer found that the thiocyanates are easily nitrified by soil, whereas thiourea resisted nitrification for three years. J. Chem. Soc. (London), Trans., **49**, 638 (1886).

After twenty-three days the following numbers for N_2O_3 were obtained :

Solution.	Milligrams N_2O_3.
1	10.0
2	8.0
3	0.20
4	None

No. 4 also gave no reaction with diphenylamine. It would seem, therefore, that in the conduct of the nitrifying organisms of the soil towards ammonium sulphocyanate and thiourea, we have an interesting confirmation of the observations of Omeliansky.[1]   According to this observer the nitrogen of organic compounds is not directly attacked by the nitrifying organisms, but must first be converted into ammonia.   It is known that urea is very readily hydrolyzed by bacteria, yielding ammonium carbonate, a compound which would readily undergo nitrification in the presence of soil organisms.   On the other hand, thiourea is hydrolyzed with great difficulty. By the action of hydrolyzing agents it is transformed into its isomer ammonium sulphocyanate, but even this change does not seem to be brought about by water alone or in the organism.   Hence we find that while ammonium sulphocyanate is slowly nitrified, thiourea is not acted on by the organisms of the soil, or if so, then only with extreme slowness as compared with ammonium sulphocyanate.

In this connection some observations on the oxidation of ammonium sulphocyanate and thiourea by hydrogen peroxide are not without interest.   In the course of some experiments on the oxidation of ammonium salts by hydrogen peroxide, one of us, Elvove, has observed that nitrites are formed from ammonium salts by the action of hydrogen peroxide, provided there is present a third substance which is capable of liberating some free ammonia, such as sodium or calcium carbonate, or an oxygen carrier, such as manganous chloride, and that in the presence of the two classes of substances the amount of nitrite produced is much greater than the sum of the amounts of nitrite produced in the presence of either alone.   It there-

[1] Centrbl., 1899, II, 347.

fore occurred to us to test the conduct of ammonium sulpho-
cyanate and thiourea towards hydrogen peroxide in the pres-
ence of calcium carbonate alone and in the presence of both
calcium carbonate and manganous chloride. Four tubes were
prepared as follows :

No. 1 contained 0.2 gram calcium carbonate, 0.1 gram am-
monium sulphocyanate, and 5 cc. of a one per cent. solution
of hydrogen peroxide.

No. 2 was same as No. 1, except that it contained in addi-
tion 0.1 gram manganous chloride.

No. 3 was same as No. 1, except that it contained 0.1 gram
thiourea, instead of the ammonium sulphocyanate of No. 1.

No. 4 was same as No. 3, except that it contained, in addi-
tion, 0.1 gram manganous chloride.

After standing at ordinary temperature for fifteen hours,
the following results were obtained :

No. of experiment.	Milligrams N_2O_3.
1	0.03
2	0.10
3	None
4	"

It is thus seen that in the case of thiourea no nitrite is pro-
duced, even in the presence of both calcium carbonate and
manganous chloride, whereas ammonium sulphocyanate under
the same conditions produces quite a measurable quantity of
nitrite. That these isomers behave differently towards hydro-
gen peroxide just as they behave differently as sources of ni-
trogen for fungi and microrganisms is certainly interesting
and significant.

A similar study of other isomeric nitrogen compounds as
sources of nitrogen to the growing plant is now being carried
on in this laboratory.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, KENTUCKY,
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THE SPECIFIC GRAVITIES OF LITHIUM CHLORIDE, BROMIDE, AND IODIDE.

By Gregory Paul Baxter.

Accurate determinations of the specific gravities of salts are very rare.[1] Furthermore, owing to almost entire lack of mention of the methods employed or the data obtained, it is seldom possible to decide how much dependence to place upon a given value. It seems worth while, then, to publish the following determinations of the specific gravities of some common salts, with full particulars concerning the methods of preparing the material and the carrying out of the determinations.

The three halides of lithium were made from lithium carbonate. This salt was obtained in a pure state by first boiling a solution of lithium carbonate in nitric acid with an excess of the carbonate, in order to precipitate all metals except those of the alkalies. Sodium and potassium were then eliminated from the filtered solution by double precipitation of the lithium as carbonate by means of ammonium carbonate. The precipitate was washed with water several times after each precipitation. When examined upon a platinum wire in the Bunsen flame no evidence of sodium was visible to the naked eye, although spectroscopically traces of this metal could be detected. The purified lithium carbonate was converted into the halides by solution in the corresponding halogen acids.

Hydrochloric acid was purified by distillation, with the use of a platinum condenser, the distillate being collected in a platinum dish. Hydrobromic acid, which had been prepared by Mr. J. B. Churchill, was similarly treated. The bromine from which this acid was made had been freed from chlorine by solution in aqueous calcium bromide and subsequent distillation. By means of red phosphorus and water the bromine was converted into hydrobromic acid and the acid was distilled to free it from the excess of bromine and any iodine

[1] See Richards and Rogers: Proc. Amer. Acad., **31**, 163 ; Baxter and Hines : This Journal, **31**, 220 (1904) ; Baxter and Lamb : *Ibid.*, **31**, 229 (1904).

which it contained, as well as from phosphoric acid. Finally, one of the middle fractions of the acid was distilled, as stated above, with a platinum condenser.

The preparation of pure hydriodic acid was a somewhat more difficult undertaking. The method ordinarily employed to free iodine from chlorine and bromine, that of sublimation from potassium iodide, is a troublesome process, hence Stas' method of distilling the iodine from aqueous potassic iodide was used. A considerable quantity of iodine was dissolved in a concentrated solution of potassium iodide, and the solution was boiled in a retort, the neck of which delivered into a flask packed in ice. Although at first the iodine condensed on the neck of the retort, no difficulty was experienced through clogging, and eventually the current of steam carried all the iodine into the condensing-flask. With equal ease the iodine was again distilled from pure water. Chlorine and bromine must be removed by this method at least as completely as by the method of sublimation, while the process requires not one-quarter the time ordinarily consumed in subliming the substance. The iodine obtained in this way is hopelessly moist, so that it could not be used for purposes of standardization without sublimation and drying, but since it was next converted into hydriodic acid by means of water and sulphuretted hydrogen, moisture was no disadvantage here. The precipitated sulphur was removed by filtration after the excess of sulphuretted hydrogen had been eliminated by boiling for several hours. During the boiling, any hydrocyanic acid resulting from cyanogen impurities in the iodine, must have been removed,[1] although it is improbable that any considerable amount of iodide of cyanogen could have resisted the potassium iodide treatment. Since the hydriodic acid was found to contain sulphuric acid, a small quantity of recrystallized barium hydroxide was added and the precipitated barium sulphate was filtered out. Finally, in order to free the acid from alkaline metals, it was distilled with a platinum condenser. Partial decomposition of the hydriodic acid, with

[1] Richards and Singer found that hydrochloric acid may be completely freed from hydrocyanic acid by prolonged boiling. This JOURNAL, **27**, 205.

liberation of iodine, took place during the distillation, so that a trace of platinum was dissolved from the condenser. The iodine and platinum were easily removed, however, in a way to be described presently.

A similar method may be advantageously used to prepare pure hydrobromic acid. Richards and Wells, working in this laboratory, have found that, if hydrobromic acid has been made by the action of bromine on red phosphorus and water, it is difficult to free the acid from last traces of phosphorus by distillation. But in a specimen of hydrobromic acid, carefully prepared after the fashion above not the least trace of sulphuric acid could be detected when the acid was diluted and treated with a considerable quantity of barium hydroxide.

From these three acids the corresponding salts of lithium were made by dissolving pure lithium carbonate in a slight excess of the acid in a platinum dish. The excess of acid was neutralized with ammonia gas and the solutions were evaporated on a steam-bath. The solid residues resulting from the evaporation of the lithium and ammonium chlorides and bromides were pure white and were used directly for the determinations. The solution of lithium and ammonium iodides was freed from platinum and iodine, in one case by heating the slightly ammoniacal solution with pure metallic iron until colorless, and then filtering the solution. In another similar sample (that used in the last determination), sulphuretted hydrogen was passed into the acid solution before the addition of ammonia, and the solution was filtered. Only a negligible amount of sulphate could have been introduced in this way. During the latter part of the evaporation the solution became yellow from the separation of a small amount of iodine. Consequently the salt was allowed to crystallize from concentrated solution, and the crystals were separated from the mother-liquor as completely as possible.

In order to dry the salts, they were fused in a platinum boat, in a current of electrolytic hydrogen. The purpose of the ammonium compounds, introduced in the preparation of the salts, was to counteract the tendency of lithium halides to become basic when heated in a moist condition. Obviously,

so long as ammonium compounds remained in the salt, the production of basic compounds was impossible. Since all but the last traces of moisture must have been eliminated before the complete volatilization of the ammonium salts, the basicity was thus reduced to a minimum.

The fusing of the salts was conducted in a tube of hard glass connected by a ground joint with a bottling apparatus by means of which the boat could be transferred, after being heated, to a weighing-bottle without exposure to moist air.[1] Heat was applied gently at first, till the greater portion of the water had been expelled, then the temperature was increased until fusion had taken place and the fused salt was limpid and free from bubbles of gas. The tube was then allowed to cool, and the boat was transferred to the weighing-bottle and weighed.

The weighing-bottle was provided with two stoppers. One was of ordinary form and was used in the weighing of the salt ; the other, which fitted the neck of the weighing-bottle exceptionally well, was provided with two capillary tubes, by means of which the bottle could be filled with any liquid. After the weighing of the salts, the ordinary stopper was removed, enough toluol to cover the boat and salt was quickly poured into the bottle, and the pycnometer stopper, which had been weighed with enough syrupy phosphoric acid to make the joint tight, was inserted. The pycnometer was placed in a vacuum-desiccator, which was then exhausted and the toluol was allowed to boil gently for a few minutes to expel the air contained in the crevices of the salt. By means of the capillary tubes the bottle was completely filled with toluol, and while the pycnometer was immersed as far as possible in a bath of water at 25°, the toluol was adjusted to a mark etched on one of the capillaries. The weight of the system was then determined. After a second adjustment of toluol, the system was again weighed. In every case the two successive weights agreed within two-tenths of a milligram. The weight of the pycnometer containing the empty boat and filled with toluol was determined

[1] Richards and Parker : Proc. Amer. Acad., **32**, 59.

three times, the extreme values of the three determinations varying only three-tenths of a milligram. From the average of these three weights, the weight of the salt and the weight of the system, including the salt and filled with toluol, was calculated the specific gravity of the salt.[1]

In one determination with each halide, the toluol from the pycnometer was evaporated, and in no case did any visible residue remain. Evidently the three salts are insoluble in toluol. The aqueous solutions of the fused salts were faintly alkaline to phenolphthalein. In Determination 7 the solution of over three grams and one-half of the iodide required eight-tenths of a cubic centimeter of N/10 acid for its neutralization, but of course this alkalinity was at a maximum in the case of the iodide. No perceptible yellow coloration was imparted to the Bunsen flame by any of the salts. Traces of sodium could be detected with the spectroscope only. Tests for ammonia with Nessler's reagent yielded negative results in the cases where they were applied. The salts were all transparent when cold, and free from gas bubbles as far as could be determined. Contraction during cooling produced cracks between the platinum and the salt, but these must have been filled with toluol during the exhaustion.

The toluol was dried by means of stick potash and was then distilled. In the following table are given the results of three determinations of its specific gravity, made with an Ostwald pycnometer, at $25°$:

	Weight of pycnometer. Grams.	Weight of pycnometer filled with water. Grams.	Weight of pycnometer filled with toluol. Grams.
	10.0868	21.3340	19.8035
	10.0868	21.3344	19.8033
	10.0867	21.3341	19.8034
Aver.,	10.0868	21.3342	19.8034

	Grams.
Weight of water	11.2474
Weight of toluol	9.7166
Density of toluol $25°/4°$	0.86152

[1] For details concerning the pycnometer and manipulation, see Baxter and Hines : This JOURNAL, **31**, 222 (1904).

In the calculations the following vacuum corrections were applied : LiCl + 0.00044 ; LiBr + 0.00021 ; LiI + 0.00015 ; toluol + 0.00126. The weights were carefully standardized to tenths of a milligram, and the corrections of the thermometer at 0° and 32°.38 were determined.

	Weight of salt in vacuum. Grams.	Weight of displaced toluol in vacuum. Gram.	Density of salt. 25°/4°.
LiCl	1.4063	0.5861	2.067
LiCl	1.7288	0.7201	2.069
		Average,	2.068
LiBr	3.0486	0.7584	3.463
LiBr	3.5161	0.8739	3.466
		Average,	3.464
LiI	3.4328	0.7283	4.061
LiI	2.2155	0.4697	4.064
LiI	3.7247	0.7905	4.059
		Average,	4.061

All of the more probable errors in these determinations, such as those due to sodium or potassium compounds, basicity, or the presence of gas bubbles in the solid, would tend to lower the observed specific gravity. Still it is highly improbable that the combined effect of all the errors could affect the second decimal figure. The specific gravities of the salts examined, at 25° referred to water at 4°, are undoubtedly very closely represented by the following numbers :[1]

Fused LiCl, 2.068 ; fused LiBr, 3.464 ; fused LiI, 4.061.

Correction.

Attention should be called to slight errors which were made in the calculations in two recent papers upon the specific

[1] Previous determinations of the densities of these salts are as follows :

LiCl	1.998	Kremers : Pogg. Ann., **99**, 62.
	2.074	Schröder : *Ibid.*, **107**, 113.
	1.515	Quincke : *Ibid.*, **138**, 141.
LiBr	3.102 at 17°,	Clarke : This JOURNAL, **3**, 13, 293.
LiI	3.485 at 23°, *Ibid.*	

gravities of cadmium and zinc salts,[1] by the assumption that the vacuum correction of the pycnometer filled with toluol was always the same whether the salt were contained or not. Obviously this is not the case ; for although the volume of the system was always the same, the weight of the system containing the salt was always greater than when it was filled with toluol only, and consequently the vacuum correction was less.   When allowance is made for this difference, the specific gravities of the salts in question become : Cadmium chloride, 4.047 ; cadmium bromide, 5.192 ; silver bromide, 6.473.   The error in the case of zinc chloride is far beyond the limit of accuracy of the experiments.

CAMBRIDGE, MASS., Jan. 6, 1904.

VII.—THE NATURE OF THE PRINCIPAL PHOSPHORUS COMPOUND IN WHEAT BRAN.

BY A. J. PATTEN AND E. B. HART.

INTRODUCTION.

From the work reported in Bulletin No. 238 of this station and from other work done preliminary to an investigation of the metabolism of phosphorus in animals, it was found that in many of our ordinary feeding-stuffs a varying percentage of the organic phosphorus was directly soluble in water and in dilute hydrochloric acid.   Data illustrating this point will be found in the following table :

Soluble Phosphorus in Oats, Malt Sprouts, and Wheat Bran.

	Solvent.	Total phosphorus. Per cent.	Soluble phosphorus. Per cent.	Percentage of total phosphorus. Per ct.
Oats	{ Water	0.355	0.180	50.0
	{ Hydrochloric		0.096	27.0
Malt sprouts	{ Water	0.677	0.548	81.0
	{ Hydrochloric		0.477	70.0
Wheat bran	{ Water	1.22	1.056	86.5
	{ Hydrochloric		0.95	77.8

[1] Baxter and Hines : " The Specific Gravities of Cadmium Chloride and Cadmium Bromide," This JOURNAL, **31**, 220; Baxter and Lamb : " The Specific Gravity of Zinc Chloride," *Ibid.*, **31**, 229.

It will be seen that wheat bran carries a much larger percentage of phosphorus than any of the others and that 86.5 per cent is soluble in water.

It was at first supposed that the soluble phosphorus was in combination as nucleins or salts of nucleic acid, but determinations of the amount of soluble nitrogen showed that only about 33 per cent of the phosphorus could be accounted for in this way.

We were therefore led to the conclusion that by far the greater part of the soluble phosphorus was linked up in some other organic combination, since Hart and Andrews[1] have shown that the amount of soluble inorganic phosphorus is exceedingly small.

Attempt to Isolate the Phosphorus Compound.

Two pounds of wheat bran were extracted with 6 liters of 0.2 per cent hydrochloric acid for several hours with frequent stirring. The extract was strained through cheese-cloth and finally filtered through paper.

The filtrate was treated with a large volume of 95 per cent alcohol which threw down a voluminous, flocculent precipitate. The precipitate was allowed to settle to the bottom, the supernatant liquid siphoned off and the precipitate washed with alcohol several times by decantation. It was then dissolved in a small volume of 0.2 per cent. hydrochloric acid, filtered from an insoluble residue, reprecipitated by alcohol, and washed as before by decantation.

This process was repeated, the precipitate finally brought upon a filter, washed with absolute alcohol and ether, and dried at 110° C. The resulting product, which weighed 7.2 grams, was a white, amorphous powder, readily soluble in water.

Its water solution was acid to litmus and it was precipitated from such solution by solutions of salts of the heavy metals, by the alkali metals and the alkaline earths, also by alcohol and ether.

Chemical analysis showed it to be an organic phosphorus

[1] Bulletin 238, N. Y. Agr. Expt. Station.

compound, coupled with calcium, magnesium, and potassium.

0.5004 gram substance gave 0.0082 gram CaO and 0.1327 gram $Mg_2P_2O_7$ equivalent to 1.13 per cent Ca and 5.80 per cent Mg.

0.512 gram substance gave 0.0834 gram K_2PtCl_6 equivalent to 2.60 per cent K.

0.2174 gram substance gave 0.1280 gram $Mg_2P_2O_7$, equivalent to 16.38 per cent P.

0.2122 gram substance gave 0.1438 gram CO_2 and 0.072 gram H_2O, equal to 18.52 per cent C and 3.83 per cent H.

The substance carried also a small amount of nitrogen (0.37 per cent), but this was considered an impurity and, calculated as a proteid, would lower the carbon and hydrogen to 17.30 per cent and 3.63 per cent respectively.

Composition of Isolated Phosphorus Compound.

	Per cent.
C	17.30
H	3.63
P	16.38
Ca	1.13
Mg	5.80
K	2.60

Similar Compounds Reported by Other Workers.

Palladin,[1] working in Schulze's laboratory, isolated from the seeds of black mustard (*Sinapis nigra*) a highly phosphorized compound in combination with calcium and magnesium.

The seeds freed from fat were extracted with 10 per cent sodium chloride solution, filtered, and the filtrate heated to about 80° C. A precipitate separated, carrying with it all of the proteid. The larger part of the precipitate went into solution again on cooling, leaving the coagulated proteid in suspension, which was separated by filtration. The filtrate was again heated and the resulting coagulum collected on a hot-water funnel.

Schulze and Winterstein[2] continued the investigation started

[1] Beitrage zur Kenntniss pflanzlicher Eiweissstoffe ; Ztschr. Biol. Jahrgang, 1894, p. 199.

[2] Ueber einen phosphorhaltigen Bestandtheil der Pflanzensamen ; Ztschr. physiol. Chem., 22, 90.

by Palladin and obtained a compound carrying 9.65 per cent carbon, 2.83 per cent hydrogen, and 16.13 per cent phosphorus. They thought the substance might be identical with the chief constituent of the globoids found enclosed in the protein kernel of many plant seeds. Pfeffer,[1] in conjunction with Brandau, found that such globoids consist of a calcium-magnesium salt of an organic body coupled with phosphoric acid. What the nature of this organic combination was they were unable to say.

Winterstein[2] isolated a compound from the seeds of black mustard by extracting with dilute acetic acid. The extract was freed from proteid by boiling and filtering when cold. The filtrate was made slightly alkaline with ammonium hydroxide and boiled, the resulting precipitate collected on a hot-water funnel and washed with hot water until the wash-water reacted neutral. The substance was purified by dissolving in dilute acetic acid and reprecipitating with ammonium hydroxide. On removing the calcium with oxalic acid, a product was obtained carrying 18.44 per cent phosphorus and 7.83 per cent magnesium.

By heating the magnesium salt in a closed tube with concentrated hydrochloric acid for thirty hours, at a temperature of 130°–140°, he obtained inosite as a cleavage-product.

The compound obtained by us from bran by the alcohol method, though still impure, is undoubtedly identical with the one described by these investigators.

Posternak[3] isolated the compound from the seeds of red fir, pumpkin, peas, beans, white and yellow lupine, and also from the potato. He also isolated and identified the free acid as anhydrooxymethylenediphosphoric acid with the following formula :

[1] W. Pfeffer: Untersuchung ueber die Proteinkoerner und die Bedeutung des Asparagins beim Keimen der Samen ; Jahrbücher für wissenschaftliche Botanik, **8**, 147 (1872).

[2] Ueber einen phosphorhaltigen Pflanzenbestandtheil, welcher by der Spaltung Inosit liefert ; Ber. d. chem. Ges., **30**, 2299.

[3] Revue Générale de Botanique, **12**, 5 and 65, 1900; Compt. rend., **137**, No. 3 (20 Juillet, 1903) ; No. 5 (3 Août 1903) No. 8 (24 Août 1903).

$$\begin{array}{c}
\text{H} \\
\diagup \\
\text{CH}\text{———}\text{O.PO(OH)}_2 \\
\diagup \\
\text{O} \\
\diagdown \\
\text{CH}\text{———}\text{O.PO(OH)}_2 \\
\diagdown \\
\text{H}
\end{array}$$
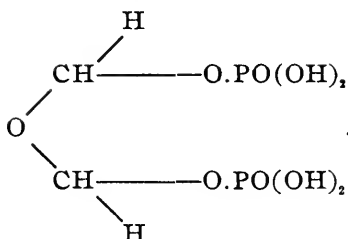
The method adopted by Posternak was the following :

The material was extracted with dilute hydrochloric acid and filtered, the filtrate made alkaline with sodium hydroxide and precipitated with calcium chloride. The calcium chloride precipitate was filtered, washed, and finally dissolved in dilute hydrochloric acid. Sodium acetate was added to the solution to replace the free mineral acid by acetic acid, and copper acetate added in excess. The copper precipitate was filtered, thoroughly washed with water, and decomposed by hydrogen sulphide.

The copper sulphide was removed by filtration and the excess of hydrogen sulphide removed by pumping air through the liquid. It was then evaporated in a vacuum over sulphuric acid.

We found it very difficult to remove the last traces of calcium by this method and have modified it by substituting barium chloride for calcium chloride. This admits of a very thorough washing at this stage of the operation as the barium salt is much more insoluble than the calcium salt, and also admits of a complete removal of the barium as a sulphate.

Method of Preparation of Free Acid.

The method finally adopted by us is as follows :

The bran was extracted with 0.2 per cent hydrochloric acid, strained through cheese-cloth and filtered through paper. Since the compound is present in bran as a calcium-magnesium-potassium salt, it was precipitated directly with copper acetate, by which means we were able to remove the greater part of these bases. After washing the copper precipitate it was suspended in water and decomposed by hydrogen sul-

phide. The filtrate from copper sulphide was made alkaline with sodium hydroxide and precipitated with barium chloride. The barium salt was washed until free from alkali, suspended in water, and dilute sulphuric acid added in sufficient quantity to decompose the salt and throw down the barium as a sulphate. After removal of the barium sulphate by filtration the filtrate was again precipitated in alkaline solution with barium chloride and treated as before. This process was repeated a third time and after final removal of the barium, copper acetate was added in excess. The copper precipitate was filtered at the pump, thoroughly washed with water, and finally suspended in water and decomposed by hydrogen sulphide. The copper sulphide was removed by filtration and the filtrate evaporated on the water-bath to a syrupy consistency.

Analysis of the acid dried at 110° gave the following results:

0.7207 gram substance gave 0.2811 gram CO_2 and 0.2202 gram H_2O equivalent to 10.63 per cent C and 3.38 per cent H.

0.1039 gram substance gave 0.097 gram $Mg_2P_2O_7$ equivalent to 25.98 per cent P.

	Calculated for $C_2H_8P_2O_9$.	Found.
C	10.08	10.63
H	3.36	3.38
P	26.07	25.98

Decomposition of Compound into Inosite and Phosphoric Acid.

Heated with concentrated mineral acids it is broken up quantitatively into inosite and phosphoric acid, according to the following equation :

$$3C_2H_8P_2O_9 + 3H_2O = (CHOH)_6 + 6H_3PO_4.$$
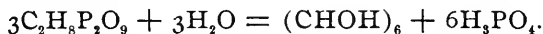
Posternak obtained 97.8 per cent of the total carbon of the acid decomposed as inosite. In our investigation an unweighed portion of the acid was heated in a closed tube with 50 cc. of 30 per cent sulphuric acid at a temperature of 155° to 160° for five hours. After cooling, the tube was opened and the contents washed into a beaker. The sulphuric and phosphoric acids were removed by barium hydroxide and the excess of barium by carbon dioxide. The filtrate was evapo-

rated nearly to dryness, taken up with hot water, and filtered from the remaining barium carbonate. The filtrate was then treated with absolute alcohol and ether until a cloudiness was produced, when it was allowed to stand in the cold. A crystalline precipitate soon separated which was obtained pure after once recrystallizing. It gave the reactions of Scherer and Gallois and melted at 218° to 219° (uncorr.). Inosite melts at 218° (uncorr.).

Carbon and hydrogen determinations were made on the substance dried at 110°.

	Calculated for $C_6H_{12}O_6$.	Found.
C	40.00	39.59
H	6.66	6.78

Properties of Anhydrooxymethylenediphosphoric Acid.

The free acid dried slowly over sulphuric acid is a very thick, transparent liquid, of a yellowish-brown color. It is soluble in all proportions in water and alcohol ; insoluble in ether, benzene, chloroform, and glacial acetic acid. It has a very sharp acid taste. Heated to 110° it becomes decidedly brown without decomposition. The alkali salts of the acid are freely soluble in water. Water solutions of the free acid are precipitated by ferric chloride, the precipitate being soluble in an excess of the reagent. Silver nitrate precipitates solutions of the free acid only after a liberal excess of the reagent has been added. The precipitate is insoluble in excess of the reagent. The free acid is not precipitated by the chlorides of magnesium, calcium, barium, or strontium, on account of the liberation of free hydrochloric acid. However, when solutions of the alkaline salts of the free acid are treated with the above reagents a precipitate is formed.

The magnesium and calcium salts are somewhat soluble in water, the barium and strontium salts very sparingly soluble. The magnesium salt is easily soluble in acetic acid, the calcium salt less so, while the barium and strontium salts are very insoluble. All are readily soluble in mineral acids.

The free acid is tetrabasic and forms two salts, the one a normal salt, the other an acid salt. The normal salt reacts ·

neutral to phenolphthalein, while the acid salt reacts neutral to methyl orange, which may be shown by the following determinations :   Ten cc. of a solution containing 0.0648 gram of the acid titrated to phenolphthalein with decinormal barium hydroxide required 10.9 cc. or 0.0748 gram barium.   0.0648 gram of the acid should require 0.0749 gram barium to produce the normal salt, $C_2H_4P_2O_9Ba_2$.   Ten cc. of the same solution titrated to methyl orange with decinormal barium hydroxide required 5.1 cc. or 0.035 gram barium.   0.0648 gram of the acid should require 0.0343 gram barium to produce the acid salt, $C_2H_6P_2O_9Ba$.

Quantitative Estimation of the Acid in Wheat Bran.

We extracted 10 grams of bran to 500 cc. with 0.2 per cent hydrochloric acid, made 100 cc. alkaline with sodium hydroxide, precipitated with barium chloride, filtered, and washed free from alkali.

The phosphorus was determined directly in this precipitate.

Total phosphorus. Per cent.	Phosphorus in barium precipitate. Per cent.	Percentage of phosphorus in barium precipitate to total phosphorus. Per cent.
1.35	0.92	68.1

Practically all of the phosphorus soluble in 0.2 per cent hydrochloric acid is in this form, as shown below :

Total soluble phosphorus. Per cent.	Phosphorus in barium precipitate. Per cent.	Percentage of phosphorus in barium precipitate to total soluble phosphorus. Per cent.
0.94	0.92	97.9

Summary.

1. Practically all of the soluble phosphorus of wheat bran is of an organic nature.

2. The organic compound exists in the bran itself as a magnesium-calcium-potassium salt of a phospho-organic acid.

3. The free acid corresponds to the formula $C_2H_8P_2O_9$, and is probably identical with Posternak's anhydrooxymethylene-diphosphoric acid.

4. The alkali salts of this acid are freely soluble in water.

The calcium and copper salts are slightly soluble, while the barium and strontium salts are but sparingly so.

5. The acid and its salts seem to be of wide distribution in the vegetable kingdom, having already been isolated from the seeds of red fir, peas, beans, pumpkin, red and yellow lupine, also from the potato and other tubers and bulbs.

In conclusion we wish to say that this forms part of the research on the metabolism of phosphorus and sulphur in the animal body conducted under the direction of Dr. Jordan. The physiological rôle of the acid and its salts in animal metabolism will be made the subject of future researches.

A NEW REDUCING-AGENT FOR THE PREPARATION OF THIOPHENOL.

By W. P. Winter.[1]

In the summer of 1903 the writer was engaged in preparing in the Chemical Laboratory of the Johns Hopkins University a considerable quantity of thiophenol for use in investigations now in progress. The main features of the method of Otto,[2] proposed in 1877, were followed. Benzenesulphone chloride is allowed to flow slowly into a small flask containing zinc dust and hot water. The zinc salt of benzenesulphinic acid which is thus formed is transferred to a large flask, and the reduction to phenyl disulphide effected at low temperature by nascent hydrogen. Better yields are obtained by allowing the mass at this stage to stand twelve hours or more with excess of granulated zinc or zinc dust. The flask is then heated for several hours on the water-bath with an excess of zinc whereby zinc thiophenolate is formed. Upon acidifying with a large excess of acid and distillation with steam, thiophenol passes over. Notwithstanding the great consumption of time and material, this method is quite superior to others that have been proposed. An outline of the best known methods is here given in historical sequence.

Voigt,[3] in 1861, published a method of reducing benzene-

[1] The writer is under deep obligation to Dr. J. C. W. Frazer for valuable suggestions and assistance in the work described in this paper.

[2] Ber. d. chem. Ges., **10**, 3055.

[3] Ann. Chem. (Liebig), **119**, 144.

sulphone chloride with nascent hydrogen. He was endeavoring to obtain benzenesulphinic acid. The sulphone chloride was allowed to drop directly on the zinc and acid mixture. One great disadvantage was that a firmly adhering mass was formed which prevented rapid evolution of hydrogen. After allowing the mass to stand twenty-four hours he distilled it and found in the receiver an oily product which he named '' benzyl mercaptan,'' while phenyl disulphide remained in the flask.

Otto says the yield of thiophenol was very moderate, and Stenhouse ascribed the fearful odor mentioned by Voigt to traces of phosphorus compounds formed in the preparation of the sulphone chloride.

Voigt stated that the boiling-point was near 165°, and he correctly described the properties of the substance, *viz.*, insoluble in water, soluble in ether, alcohol, benzene, and carbon bisulphide. It burns with a white flame ; produces blisters, difficult to heal, on the skin ; the vapor attacks the eyes, while prolonged exposure to it produces dizziness. It forms a number of salts with the heavy metals, and dissolves sulphur and iodine. Heated with strong nitric acid it combines, somewhat violently, to form phenyl disulphide.

Otto,[1] in 1867, attempted to reduce sulphophenylethylene, $C_6H_4SO_2C_2H_4$, with nascent hydrogen, thinking he would obtain a mixed sulphide, $C_6H_5SC_2H_5$, but he obtained instead thiophenol and ethyl alcohol. His method was similar to Voigt's. He described the boiling-point as between 170° and 175°.

Kekulé and Szuch,[2] in 1867, showed that if phenol and phosphorus pentasulphide are heated in certain proportions the principal product is thiophenol. Five hundred grams of phenol yield 30 grams of thiophenol, or about 6 per cent of the phenol used. An increase of the pentasulphide beyond the proportion of 10 molecules of phenol to 1 of the pentasulphide diminishes the yield. Moreover, it is quite impossible to separate traces of phenol from the product. They gave the boiling-point as 167° or 168°.

[1] Ann. Chem. (Liebig), **143**, 205.
[2] Ztschr. Chem., **193**, 300 (1867).

Stenhouse,[1] in 1869, distilled sodium benzenesulphonate in iron retorts. He obtained " phenyl mercaptan," C_6H_5SH, in the portion of the distillate coming over between 165° and 180°, and after redistilling from glass the product attained the constant boiling-point of 172°.5. Phenyl disulphide comes over above 180°, and he observed that this could be reduced to thiophenol by zinc and acid, or, better, by digestion with amorphous phosphorus and hydriodic acid.

Stadler,[2] in 1884, distilled sodium benzenesulphonate slowly in a vacuum with a little more than the equivalent amount of potassium hydrosulphide. Out of 10 grams of the material he obtained a yield of 2.5 grams of thiophenol, while the theoretical amount is 6 grams. Attempts to use larger quantities at one time gave smaller yields. The author commends the method for its rapidity and simplicity rather than for the yield it affords.

In 1886, Otto and Rossing[3] found that on warming phenyl disulphide with potassium sulphide in alcoholic solution there was an almost immediate formation of potassium phenylmercaptide. On treating this with hydrochloric acid and distilling with steam, they obtained free thiophenol. Potassium disulphide, K_2S_2, has no action on phenyl disulphide.

Friedel and Crafts,[4] in 1888, showed that if benzene and powdered sulphur are heated in the presence of aluminium chloride to 75° or 80° until the evolution of hydrochloric acid and hydrogen sulphide ceases, and the mixture is then poured into water, an oily supernatant layer separates which by fractional distillation is separable into three portions : the first, phenyl mercaptan (boiling-point 170° to 173°) ; the second, phenyl disulphide (boiling-point 288°) ; the third, diphenylene disulphide (boiling at 364°).

In 1890, Leuckart[5] based a method on the use of phenyl ethyl dithiocarbonate, formed by the interaction of diazobenzene chloride and potassium ethyl dithiocarbonate. This was boiled with alcoholic potash until the solution remained clear

[1] Ann. Chem. (Liebig), **149**, 247.
[2] Ber. d. chem. Ges., **17**, 2080.
[3] *Ibid.*, **19**, 3129.
[4] Ann. chim. phys. [6], **14**, 437.
[5] J. prakt. Chem., [2], **41**, 187.

on addition of water. The alcohol was removed by distillation, water was added to dissolve the residue, and also zinc dust and acid to prevent oxidation. When steam was passed through, thiophenol came over. The yield was 70 per cent of the theoretical, 7 grams of thiophenol being obtained from 20 grams of ester. The author states that large quantities can be prepared at one time as it is not necessary to purify the ester.

Turning now to the practical laboratory method for the preparation of thiophenol which is most followed, namely, the "Otto method" already mentioned, the chief difficulties encountered were that the low yield and the time involved in carrying through one portion make the production of any considerable amount tedious. The yield seems to be affected by minor details to an unusual degree. Theory requires nearly 30 grams for each 45 grams of benzenesulphone chloride instead of the 18 to 22 grams usually obtained.

Without detailing the many variations of this stock method which were employed in the hope of improving the process, it is sufficient to state that no manipulation of the details of the process by several workers in this laboratory, who have had occasion to prepare large amounts of thiophenol, has succeeded in bringing about the desired yield.

It was at this stage that the suggestion was made to try other reducing agents, and the work was carried on nearly simultaneously with several such agents until a modification of the original method was devised which gave better results.

An account of the reducing agents which proved unsatisfactory is first given in the belief that by some, at least, negative results are valued for the light they throw on the purely scientific as contrasted with the technical side of the subject. It was found that the first step of the reaction could not be advantageously changed. When either iron filings, granulated tin, or tin in a finely divided state was employed to combine with the benzenesulphone chloride, the yield was always inferior to that by the old process. Hence the first step was the formation of zinc benzenesulphinate in the usual way. Iron turnings were tried in the second stage, namely, the re-

duction of the zinc sulphinate to phenyl disulphide, but with indifferent results. Ordinary granulated tin at this point produced a somewhat better yield but still inferior to that of zinc dust. Finely divided tin produced by the action of zinc upon a solution of stannous chloride was more promising, producing, in some cases, a yield equal to that of the old method.

Stannous chloride was then used in the same manner and amount as zinc dust by the Otto method with satisfactory results. It was found that the subsequent heating on the water-bath could be shortened to about one-half hour, and that the use of a small quantity of zinc dust (about 60 grams) at this stage exerted a beneficial action.

While the intermediate products of the reaction were not examined, the behavior of the material in the flask seemed to show that, in all probability, there is more direct reduction to the end product, little phenyl disulphide being formed. The difficulty of the complete reduction of the salts of phenyl disulphide seems to stand in the way of the theoretical yield by the old process. But that a little phenyl disulphide is formed, even when stannous chloride is used, is shown by the fact that the addition of a small amount of zinc dust at the latter part of the second stage of the process results in an increased yield (see appended table).

When the flask has cooled, a moderate excess of hydrochloric acid is added and the mixture is distilled with steam. Practically all the thiophenol comes over in the first 100 or 200 cc.

As the tin is thrown out of the solution in the spongy condition by the addition of zinc dust, it is practicable when working on the large scale to reconvert it into stannous chloride for subsequent use. The yield of thiophenol obtained was practically theoretical.

The following table shows the comparative yields of crude thiophenol obtained for each 45 grams of benzenesulphone chloride :

	Thiophenol in grams.
Otto process (zinc dust)	19.5
" " " "	22.0
" " " "	22.5
" " " "	22.5
" " " "	20.0
" " " "	20.0
" " " "	22.0
" " " "	20.0
" " " "	20.0
Fe as reducing agent	10.0
Granulated Sn "	13.5
" " "	19.5
Finely divided Sn	18.0
" " "	19.5
" " "	20.0
SnCl$_2$ without zinc dust	25.5
" " " "	22.5
" " " "	20.0
" " " "	23.5
" " " "	24.5
SnCl$_2$ with zinc dust	28.5
" " " "	30.5
" " " "	30.5
" " " "	27.5
" " " "	26.0

CXVII.—ON ISOMERISM IN THE AMIDINE SERIES : DIPHENYLBENZENYLAMINOAMIDINE AND PHENYLBENZENYLPHENYLAMINO-AMIDINE.

By HENRY L. WHEELER AND TREAT B. JOHNSON.

Of the large number of chemists that have had occasion to deal with amidines probably no one has more carefully or more thoroughly investigated the question of their isomerism than von Pechmann. Among his last words on this subject[1] may be found the statement " dass die bekannten Methoden zur Darstellung der beiden stellungsisomeren Amidine,

$$RC{\diagup}^{NX}_{\diagdown NHY} \qquad\qquad RC{\diagup}^{NHX}_{\diagdown NY} ,$$
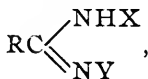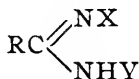
[1] Ber. d. chem. Ges., **30**, 1779 (1895).

immer zu einem einzigen Product führen, obwohl Bildungs-
weisen und Formeln je zwei verschiedenen Verbindungen
erwarten lassen.''

This statement is just as true to-day as it was nine years
ago when the above was written.   When, therefore, Acree[1]
described his so-called 1-phenyl-2-hydro-3-ethoxyurazole, in-
soluble in alkalies, Formula I., and called attention to the
fact that the isomeric compound, II., soluble in alkalies had
been made by Wheeler, we concluded that Acree was mistaken
in regard to his compound.   This result of Acree's being im-
portant, if true, we, therefore, prepared the compound, insol-
uble in alkali, precisely according to his directions and found,
as we suspected, that it was not a monoethoxy but a diethoxy
derivative,[2] Formula III.

$$C_6H_5N\text{----}NH$$
$$OC \qquad COC_2H_5$$
$$N$$
I.

$$C_6H_5N\text{----}N$$
$$OC \qquad COC_2H_5$$
$$NH$$
II.

$$C_6H_5N\text{----}N$$
$$C_2H_5OC \qquad COC_2H_5$$
$$N$$
III.
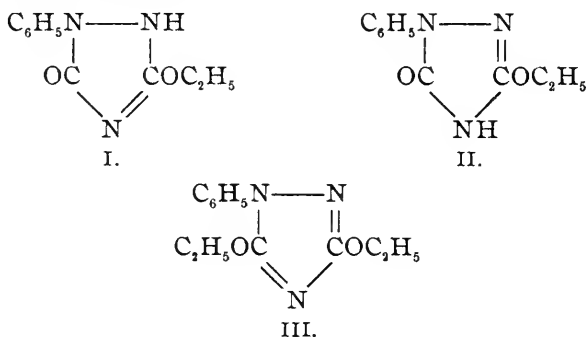
This, therefore, was no exception to the usual experience
that such formulas as I. and II. represent a single chemical
individual.   In a recent note[3] on some of the reactions in the
urazole series Acree discusses this point and makes a number
of misleading and incorrect statements, not only in regard to
our work,[4] but also in connection with the theoretical side of

[1] This JOURNAL, **27**, 120 (1902).

[2] We take this occasion to thank Professor M. M. Richter for calling our attention
to the fact that the compound described by Acree (*loc. cit.*) as a dicarbethoxysemi_
carbazide, and which we showed was a monocarbethoxy derivative, had already
been described by Rupe. Ber. d. chem. Ges., **32**, 12 (1899).

[3] This JOURNAL, **31**, 185 (1904).

[4] Being convinced of the accuracy of our results as published in our paper on the
molecular rearrangement of amido acid anhydrides (This JOURNAL, **30**, 24 (1903)), and
having obtained the data we were looking for, we see no occasion either to repeat
our work, as suggested by Acree, or to further discuss the results there described.

the subject. For example, he states: "The possibility of this kind of isomerism is proved beyond question by the isolation of just such tautomeric benzenyldiphenylhydrazidines and the tautomeric methenylphenyltolylamidines."

Now, let us examine the references he quotes and certain facts in connection with them. They point in a most emphatic manner to a precisely opposite conclusion.

The first is, curiously enough, to von Pechmann's work in which no case of isomeric benzenyldiphenylhydrazidines occurs whatever, but in the summary of this article von Pechmann states that compounds of the type I. and II. have identical physical and chemical properties, and that they exist in fact in only one form,[1] etc.

Another reference is to Walther's[2] four supposed isomeric methenylphenyltolylamidines, which we have thoroughly examined, and in three papers from this laboratory[3] we showed that these compounds do not exist but are, without exception, mixtures. Our work, in fact, has proved beyond question that only one methenylphenyl-p-tolylamidine exists at present. This fact has been recognized by von Pechmann and others.

The remaining reference[4] deals with the only case in which von Pechmann observed the formation of isomers when an imide chloride was treated with a base. This unexplained result of von Pechmann's is the only point that deserves further attention in Acree's note.

Von Pechmann states that by the action of phenylhydrazine on benzanilideimide chloride two isomeric amidines were obtained which he provisionally represented as follows:
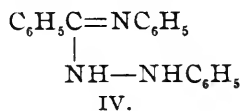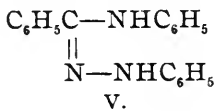
$$C_6H_5C=NC_6H_5 \qquad\qquad C_6H_5C-NHC_6H_5$$
$$| \qquad\qquad\qquad || $$
$$NH-NHC_6H_5 \qquad\qquad N-NHC_6H_5$$
$$IV. \qquad\qquad\qquad V.$$
$$m.\ p.\ 174°. \qquad\qquad m.\ p.\ 119°.$$

[1] Ber. d. chem. Ges., **28**, 869.

[2] J. prakt. Chem., **55**, 41 (1897).

[3] This JOURNAL, **19**, 367 (1897); *Ibid.*, **20**, 853 (1898); Ber. d. chem. Ges., **32**, 35 (1899).

[4] Ber. d. chem. Ges., **28**, 2362.

In the very next paragraph he cites arguments to show that these amidines are not to be represented as above, and ends by saying that it must be left undecided in what manner these isomeric amidines are to be represented. He states that tautomerism is excluded here. The above, nevertheless, illustrates how, according to Acree, '' the possibility of this kind of tautomerism is proved beyond question.''

Of course we do not maintain that such cases of tautomerism or rather desmotropism are impossible but, in view of the careful work of von Pechmann and others all assumed isomers of this sort should be viewed with suspicion and deserve examination.

An examination of the properties of the above isomeric amidines of von Pechmann showed that the substances differed decidedly in properties. It suggested to us that the isomerism was due to decided structural differences. It was noteworthy that when benzphenylhydrazideimide chloride was treated with aniline only the high-melting compound was obtained. This, therefore, must have the benzenyl group attached as shown in Formula IV. or V. That isomers resulted in the other case was believed to be due to the fact that phenylhydrazine offers two points of attack to benzanilideimide chloride, as it has frequently been observed to do in the case of other reactive substances,[1] so that in addition to the above, the following compound, VI., would result :

$$C_6H_5C=NC_6H_5 \qquad C_6H_5C=O \qquad C_6H_5C=O$$
$$H_2N—NC_6H_5 \qquad H_2N—NC_6H_5 \qquad NH—NHC_6H_5$$
$$\text{VI.} \qquad\qquad \text{VII.} \qquad\qquad \text{VIII.}$$
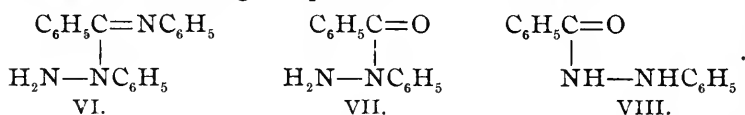
A comparison of the properties of these amidines with those of the corresponding benzoylphenylhydrazines then showed a striking similarity. Unsymmetrical benzoylphenylhydrazine, VII., melts lower than the symmetrical and is not affected by mercuric oxide ; the low-melting amidine behaves in like manner. The low-melting compounds in both cases are most basic. The high-melting amidine and symmetrical benzoylphenylhydrazine are both oxidized by mercuric oxide, etc.

[1] Busch : Ber. d. chem. Ges., **34**, 322 (1901) ; *Ibid.*, **36**, 3877 (1903) ; Frerichs and Beckurts : Arch. Pharm., **237**, 346 (1899).

Busch and Holzmann[1] have shown that the corresponding unsymmetrical diphenylthiosemicarbazide gives thiocarbanilide with nitrous acid just as Michaelis and Schmidt[2] have shown that unsymmetrical benzoylphenylhydrazine gives benzanilide under similar treatment ; we therefore submitted the low-melting amidine to the action of nitrous acid, whereupon evolution of gas took place and benzenyldiphenylamidine was quantitatively obtained :

$$
\begin{array}{ccc}
C_6H_5C{=}NC_6H_5 & & C_6H_5C{=}NC_6H_5 \\
| & \longrightarrow & | \\
H_2N{-}NC_6H_5 & & HNC_6H_5 \\
VI. & &
\end{array}
$$
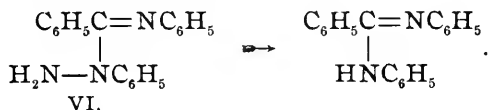
This proves beyond question that the lower-melting amidine has the structure represented by formula VI., and since tautomerism is excluded in this case the isomeric amidine melting at 174° must be represented by formula IV. or V. ; either one will suffice.

The ease with which the high-melting amidine is oxidized by mercuric oxide is in better accord with formula IV. The oxidation, however, may involve a " 1,4-Abspaltung " of hydrogen from structure V., similar to that observed by Thiele[3] in the removal of bromine from other unsaturated compounds. We have found that this amidine reacts immediately and quantitatively with phosgene, giving 1,3,4-triphenyl-1,2,4-triazolone, identical with the substance recently obtained by Busch and Walter[4] by oxidizing benzaldehyde-2,4-diphenyl-semicarbazone. This result is most simply explained by considering the structure to be represented by formula V., the reaction being as follows :

$$
\begin{array}{c}
C_6H_5C{-}NHC_6H_5 \\
\| \\
N{-}NHC_6H_5
\end{array}
+ COCl_2 =
\begin{array}{c}
C_6H_5C{-}NC_6H_5 \\
\| \quad \quad {>}CO \\
N{-}NC_6H_5
\end{array}
+ 2HCl.
$$
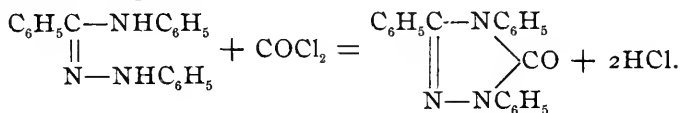
To be sure we can assign formula IV. to the amidine, then in this reaction the phosgene must react by addition to the tertiary nitrogen atom.

[1] Ber. d. chem. Ges., **34**, 323 (1901).
[2] Ann. Chem. (Liebig), **252**, 317 (1889).
[3] *Ibid.*, **306**, 108.
[4] Ber. d. chem. Ges., **36**, 1360 (1903).

At any rate the reactions with nitrous acid and phosgene, alone, are sufficient to show that the amidines are structurally different and are not tautomeric or desmotropic forms. In accordance with the fact that the substances are not tautomeric they give different products with various reagents, nitrous acid, phenyl mustard oil, etc. Moreover, if the substances were tautomeric their hydrogen chloride salts would be identical.[1]

$$RC\underset{NHY}{\overset{NX}{\diagup}} \quad \longrightarrow \quad RC\underset{NHY}{\overset{NHX}{\diagup}}Cl \quad \longleftarrow \quad RC\underset{NY}{\overset{NHX}{\diagup}} .$$
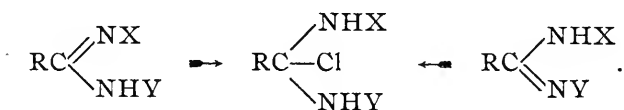
The work of von Pechmann has shown, however, that his salts differ widely in properties and therefore are not identical. With these results it is evident that desmotropism in the amidine series remains yet to be discovered.

<div align="center">EXPERIMENTAL PART.</div>

Diphenylbenzenylaminoamidine, $\begin{array}{c} C_6H_5C\!=\!NC_6H_5 \\ | \\ H_2N\!-\!NC_6H_5 \end{array}$ *and Nitrous Acid.*—Fifty grams of benzanilide and 54 grams of phosphorus pentachloride gave about 42 grams of benzanilideimide chloride boiling at $187°-190°$ at 19–20 mm. pressure. This was immediately dissolved in ligroin and 53 grams of phenylhydrazine were added ; the reaction took place quietly and a cream-colored mass of material separated. The material was dried and extracted three times with hot water. The aqueous extract, on treating with ammonia, gave 10 grams of the crude, lower-melting amidine. It was purified by crystallizing several times from alcohol, whereupon it agreed with the description given by von Pechmann.

Three grams of this material were dissolved in 20 cc. of concentrated hydrochloric acid and 1 gram of potassium nitrite was dissolved in a small amount of water. When these solutions were mixed, a white precipitate separated and gas was evolved. The precipitate proved to be the difficultly soluble hydrochloride of benzenyldiphenylamidine ; this was

[1] Stieglitz : This JOURNAL, 21, 109; McCoy : *Ibid.*, 21, 132 (1899).

dissolved in hot water and then ammonia precipitated 2.6 grams of the free amidine, the calculated being 2.8 grams. When crystallized from alcohol the material formed needle-like prisms and melted sharply at 145°.

Some benzenyldiphenylamidine was prepared for comparison from benzanilideimide chloride and aniline. The material thus obtained had all the properties of the above and when portions were mixed the melting-point was not altered.

A nitrogen determination in the case of the material obtained by the action of nitrous acid gave a result agreeing with the calculated for benzenyldiphenylamidine :

	Calculated for $C_{19}H_{16}N_2$.	Found.
N	10.2	10.1

Benzoyldiphenylbenzenylaminoamidine.—A portion of the above aminoamidine was warmed in benzene with the calculated quantity of benzoic anhydride. On evaporating the benzene, washing the residue with ammonia, and then crystallizing from alcohol, colorless, rhombic plates were obtained, which melted at 136°. A nitrogen determination gave :

	Calculated for $C_{26}H_{21}ON_3$.	Found.
N	10.7	10.4

When the higher-melting amidine was treated in the same manner with benzoic anhydride a benzoyl derivative was not obtained.

Phenylbenzenylphenylaminoamidine and Phosgene. — The product which resulted on treating benzanilideimide chloride with phenylhydrazine, after being thoroughly extracted with hot water, was crystallized from a large amount of alcohol, in which it is difficultly soluble. It then agreed in properties with von Pechmann's description of his higher-melting amidine (m. p. 174°–175°).

Three grams of this material were dissolved in chloroform and about 20 cc. of 20 per cent. phosgene in toluene were added ; no precipitate was formed, but on evaporating the solvent on the steam-bath, a residue was obtained which was very difficultly soluble in alcohol, more soluble in benzene,

and still more soluble in chloroform. It formed needles from these solvents and melted at 217°–218°. It had all the properties of *1,3,4-triphenyl-1,2,4-triazolone*, which Busch and Walter[1] have prepared by another method, except that they give its melting-point at 215°–216°. A nitrogen determination gave:

	Calculated for $C_{20}H_{15}ON_3$.	Found.
N	13.41	13.23

The amidine melting at 119° unites with phenyl mustard oil with great energy. The product is a cream-colored powder, very difficultly soluble in benzene and alcohol and it shows no signs of melting at 345°. The isomeric amidine melting at 174° combines with phenyl mustard oil, but with far less energy, and an entirely different substance is formed. It is difficultly soluble in alcohol. When dissolved in chloroform and precipitated with alcohol, needles are obtained which melt at about 186°. The products were not further investigated.

NEW HAVEN, CONN., March 4, 1904.

THE SIGNIFICANCE OF THE MAXIMUM IN THE CONDUCTIVITY CURVES OF KRAUS AT HIGH TEMPERATURES.

BY HARRY C. JONES.

Two papers on the conductivity of solutions of electrolytes at high temperatures have recently appeared. A. A. Noyes and Coolidge[2] have studied the conductivities of two electrolytes in water up to 306°. They found that the conductivities increase very rapidly with rise in temperature, and also that the *dissociation decreases with rise in temperature.* The increase in conductivity with rise in temperature is, of course, due to the increase in the velocities of the ions; but the second point, the decrease in the dissociation with rise in temperature is of special interest in connection with the theory of Dutoit and Aston,[3] connecting the dissociating power of a solvent

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[1] *Loc. cit.*

[2] Ztschr. phys. Chem., **46**, 323.

[3] Compt. rend., **128**, 240 (1897).

with its own association. As the temperature rises, the water becomes less and less associated, as was shown by the work of Ramsay and Shields.[1] As the association of the water becomes less its dissociating power becomes less, and hence the decrease in the dissociation of aqueous solutions with rise in temperature.

Kraus,[2] in his investigation of solutions in methyl and ethyl alcohols, has studied the conductivities up to, through, and beyond the critical temperatures of the solvents. Kraus points out that the conductivity passes through a maximum with rise in temperature. This maximum, in the case of solutions in methyl alcohol, occurs at 150°, while in solutions in ethyl alcohol it is at about 100°. It remains to be seen whether Noyes' will find such a maximum in aqueous solutions when he studies the conductivities between 306° and the critical temperature of water. This maximum in the conductivity is of special interest and should be fully interpreted. It is obvious that the conductivity increases with rise in temperature, because the ions move faster at the higher temperature. At the same time the solvent is becoming less and less associated the higher the temperature. As the association of the solvent becomes less, its dissociating power becomes less.

We have then two influences on the conductivity with rise in temperature, and these work counter to each other. The ions move faster and faster with rise in temperature, increasing the conductivity. The association of the solvent becomes less and less with rise in temperature, and, consequently, its dissociating power becomes less and less. This, of course, diminishes the conductivity. The maximum in the conductivity curve represents the temperature at which *these opposite influences become equal.*

These maxima in the conductivity curves are of such importance that their exact significance should be clearly pointed out.

[1] Ztschr. phys. Chem., **12,** 433 (1893).
[2] Phys. Rev., **18,** 40 (1904).

REVIEWS.

A MANUAL OF QUALITATIVE CHEMICAL ANALYSIS. By J. F. Mc-
GREGORY, Professor of Chemistry and Mineralogy in Colgate Uni-
versity. Ginn and Co., 1903.

The methods of separation recommended in this book are
good, the directions are clear; it is a very satisfactory
manual for a college laboratory. The author does not print
the usual tabular schemes for analysis of the different groups,
believing that "the use of them in the hands of the majority
of students is pernicious." As the great majority of the
manuals in use employ the method of tables, its absence will
serve as a special recommendation of this book to the many
teachers who agree with Professor McGregory on this sub-
ject.   E. R.

KALENDER FÜR ELEKTROCHEMIKER, SOWIE TECHNISCHE CHEMIKER
UND PHYSIKER, 1904,

It is only necessary to call attention to the appearance of
the eighth edition of Dr. Neuberger's electrochemical calen-
dar. This useful little book is now brought up to date, and
will be welcomed by all who are interested in electrochem-
istry.   H. C. J.

DISINFECTION AND THE PRESERVATION OF FOOD. By SAMUEL RIDEAL.
New York: John Wiley & Sons. 1903.

This is a reprint of the London edition of this valuable
work. The author treats of disinfection first from a mechan-
ical point of view, next sterilization by heat, and third, chem-
ical disinfectants. Under mechanical disinfection he de-
scribes the absorption of noxious gases and liquids by char-
coal, coke, soot, coal-dust, peat, sawdust, clay, infusorial
earth, ashes and cinders, and gypsum. The subject of sand
filtration is also fully treated from the sanitary point of view.
The effect of low temperature and other dissociation is also
included under the mechanical head.

The value of heat as a disinfectant and preserver is treated
in Chapter III., in which the principles of heat disinfection
are established and the methods of applying it described.
The chemical disinfectants are treated under several different
heads : First, the halogens and their compounds ; second,
non-metallic elements and their derivatives ; third, metallic
salts, organic substances and compounds related to the alco-
hols.

Chapter XII. deals with practical methods of applying the
principles of disinfection and sterilization. It treats of sewers

and drains, sick-rooms, earth-closets, water-closets, infection by flies, furs, wool, and rags. The principles of disinfection of air, water, and its methods of purification and the preservation of timber are described.

Chapter XIII. describes personal and internal disinfection and shows that the common opinion that sachets and lockets containing odoriferous substances are useful is incorrect. The disinfection of cavities of the body is fully described and the necessity therefor accentuated. The utility of antiseptic dressing and of antiseptic hypodermic injections is discussed. Internal disinfection by means of charcoal, chlorinated soda, and sulphides is also mentioned and there is a discussion of the much-mooted question of vaccination. The author calls attention to the fact that modern research seems to indicate that toxines produced by the micro-organisms of infectious disease are the natural disinfectants for combatting it. He states that "Natural immunity is produced either by dissolved alexines or from the resistance of the tissues, whilst acquired immunity is due to the presence of modified bacterial products."

The discussion of disinfection of cuts or abrasions is of general interest since so many serious lesions and often even death are produced by a failure to observe even ordinary precautions when the cuticle is broken. The author states: "If a cut or wound has been accidentally produced, cauterizing with nitrate of silver, nitric acid, phenol, permanganate, or osmic acid is frequently recommended, but the scar left is often very painful and troublesome to heal, besides not being thoroughly safe against inoculation. Covering with lead or court-plaster, or with collodion, painting with iodine, thoroughly drying the cut and painting with a solution of Stockholm tar or Burgundy pitch in alcohol, ether, or acetone, are among the other treatments suggested. None of these give absolute immunity, so that in case of accidental puncture during a post-mortem or operation, or in handling contagious matter such as dead meat, skins, or evacuations, it is probably safest to wash immediately with mercuric chloride, dry, and at once cauterize, and thus combine the two precautionary measures."

If the author means "osmium tetroxide" by the osmic acid mentioned above, its use as a disinfectant should be attended with precautions. Its vapor is very dangerous to the lungs, it acts violently on the skin, causing painful eruptions, and produces intense inflammation of the eyes which often has serious consequences.

The chapter on the sanitary arrangement of dwelling-houses in respect of air, light, heat, wall-paper, furniture, sinks, sick-rooms, and bed-chambers cannot fail to be of great practical help.

That part of the book relative to disinfection extends to page 408 while the part relating to the preservation of food is only 30 pages. This part, whoever, gives a condensed history of the preservation of food by means of salt, niter, aromatic substances, vinegar, etc. The other common methods of preservation are described, such as smoking, salting, preserving in carbon dioxide, and the use of chemical preservatives. Attention is called to the fact that at the International Congress on Hygiene at Brussels in 1903, resolutions were adopted favoring the total abolition of preservatives in all kinds of food. The recommendations of the English Departmental Committee in regard to preservatives are given on page 423. These forbid the use of formaldehyde or formalin absolutely, permit a small quantity of salicylic acid when declared on the label except in the case of milk when no preservative of any kind is to be admitted. In cream, boric acid and borax are permitted when the amount does not exceed 0.25 per cent expressed as boric acid, the amount to be notified by a label. The same preservative is permitted to be used in butter and margarine in proportions not exceeding 0.5 per cent expressed as boric acid. In the case of all foods intended for the use of invalids or infants chemical preservatives of all kinds are prohibited.

The preservation of food by sterilization is fully described, with a brief historical statement.

Whether or not the extreme doctrine of absolute prohibition of all preservatives except those of a condimental nature should be adopted is a matter still open for discussion. Dr. Rideal's book, however, supports the conservative element in this discussion, namely, to the effect that the use of preservatives of a chemical nature, other than condiments, such as sugar, salt, etc., should be discouraged and that in all cases where foods are prepared for invalids and infants they should be prohibited and in all other cases minimum quantities should be used and notification of such use plainly stated upon the labels.

The fifteenth chapter treats of legal statutes and regulations in regard to disinfection. Chapter XVI. deals with methods of analysis which are, necessarily, of the briefest character.

This work will prove of interest both from a scientific point

of view and also in the practical application of the principles
of disinfection and food preservation.   H. W. W.

LE POINT CRITIQUE DES CORPS PURS. By PROFESSOR E. MATHIAS, of
   the University of Toulouse. pp. viii + 251. 1904. Paris : C. Naud.

This book contains useful tables of critical data, and useful
descriptions of methods of obtaining them. The theoretical
part of the book is far less satisfactory, being a forensic in
favor of the existence of heterogeneity at the critical point.
The argument is, as the author hopes, courteous, but too
much emphasis seems to be laid upon the early crude results,
and too little upon the recent work of Ramsay (1894), Young
(1897), and Villard (1897), in which the importance of an
unusual degree of purity is demonstrated. The interesting
work of Hagenbach (1901), upon dilute solutions of iodides
in sulphurous oxide is discussed at length. These results
lead Professor Mathias to admit that the supposed heteroge-
neity at the critical point is merely temporary—a theoretical
improvement upon the earlier attitude regarding it as perma-
nent—but the reviewer thinks that insufficient account is taken
of the effect of gravitation in preventing the rapid diffusion of
the iodide. This effect alone would cause delay in establish-
ing constancy in composition in the two layers of material.
Thus the work of Hagenbach really supports the other argu-
ment in favor of a single definite critical volume.   T. W. R.

THE ANALYTICAL CHEMISTRY OF URANIUM. By HARRY BREARLEY,
   joint author of "The Analysis of Steel-Works Materials." Long-
   mans, Green and Co. 1903. 45 pp.

Mr. Brearley has made a special study of the methods of
determining uranium, and their availability in the presence
of salts of other metals. This book gives the results of the
author's work, and is a valuable book for the practical
analyst.   E. R.

THE ELECTROLYSIS OF WATER ; PROCESSES AND APPLICATIONS. By
   VIKTOR ENGELHARDT, Chief Engineer and Chemist of the Siemens
   and Halske Co., Limited, Vienna. Translated by J. W. Richards,
   Lehigh University. Easton, Pa.: Chemical Publishing Co.

As the *raison d'être* for writing this book the author states
among other things, in his preface, that " The description
given (in the literature) of the form of apparatus is usually
only diagrammatic, and often has the object of *deceiving* those
who should hope to work in the same direction," and " with
the exception of the patent specifications, very little is made
public. Every practical electrochemist knows how far the

principles described in the patent specifications are different from the real applications in practice."

It is generally known that technical processes are often kept secret and with the present conceptions that obtain in such matters possibly this is necessary. But that actual *deception* is practiced in such matters must be deplored by every one with ordinary scientific instincts.

Any book which will tend to alleviate this condition of things is most welcome.   H. C. J.

TABLES FOR CHEMICAL CALCULATIONS WITH EXPLANATIONS AND ILLUSTRATIVE EXAMPLES. By HORACE L. WELLS, Professor of Analytical Chemistry and Metallurgy in the Sheffield Scientific School of Yale University. 1903. New York : Henry Holt & Company. 58 pp.

This very useful little book is one that might well be on the desk of every analytical chemist. It contains eleven tables, giving a great variety of information. Besides the usual gravimetric factors and their logarithms, atomic weights, weights of gases, barometer corrections, etc., it contains tables of analytical factors involving gas-volumes, metallurgical factors, and a long list of formula (molecular) weights and their logarithms. The table of five-place logarithms is very conveniently arranged with the edges of the pages cut in and indexed as they are in the larger dictionaries. Tables of constants for the boiling- and freezing-point methods, and one for the conversion of English weights and measures into the metric system are appended to the book. Nearly one-half the space is devoted to the explanations, which are clear and made still more so by the well-chosen examples. A few faults were noticed, but they do not detract to any great extent from the value of the book.   C. E. W.

ELECTROLYTIC PREPARATIONS. Exercises for Use in the Laboratory by Chemists and Electrochemists. By DR. KARL ELBS, Professor of Organic and Physical Chemistry at the University of Giessen. Translated by R. S. HUTTON, M.Sc., Demonstrator and Lecturer on Electrochemistry, Owens College, Manchester. London : Edward Arnold. 1903. xi + 100 pp.

The German edition of this important aid to the student of electrochemistry has already been noticed in this Journal.[1] It need only be said that the translator has done well in bringing this work within reach of those who are not familiar with the German language. The translation is good and the book is printed in a convenient size for use in the laboratory.

                                                    C. E. W.

[1] This JOURNAL, **29**, 618 (1903).

AMERICAN

CHEMICAL JOURNAL

Contributions from the Sheffield Laboratory of Yale University.

CXVI.—RESEARCHES ON PYRIMIDINE DERIVATIVES: 5-METHYLCYTOSINE.

[FIFTH PAPER.]

By Henry L. Wheeler and Treat B. Johnson.

In a previous paper we[1] showed that cytosine gives uracil on heating with acids. If uracil is to be reckoned as cytosine in the nucleic acids then 5-methyluracil or thymine possibly results by the cleavage of a corresponding base, namely, 5-methylcytosine (formula I.) or the isomeric 2-amino-5-methyl-6-oxypyrimidine (III.) :

$$
\begin{array}{ccc}
\text{N=C—NH}_2 & \text{HN—CO} & \text{HN—CO} \\
|\quad\ | & |\quad\ | & |\quad\ | \\
\text{OC}\ \ \text{CCH}_3 & \text{OC}\ \ \text{CCH}_3 & \text{H}_2\text{N—C}\ \ \text{CCH}_3 \\
|\quad\ \| & |\quad\ \| & \|\quad\ \| \\
\text{HN—CH} & \text{HN—CH} & \text{N—CH} \\
\text{I.} & \text{II.} & \text{III.}
\end{array}
$$
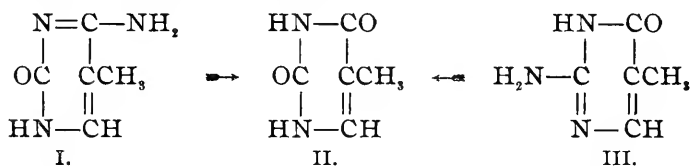
We therefore decided to prepare these new bases and to compare their properties with those of cytosine. In this paper we describe 5-methylcytosine and in a later paper by Dr. Johnson and Mr. S. H. Clapp, the compound represented by formula III. will be discussed. We prepared the compound represented by formula I. as follows : The ethyl bromide addition-product of thiourea was treated with one molecular

[1] This JOURNAL, **29**, 494 (1903).

proportion of alkali in aqueous solution and the sodium salt of ethyl formylpropionate added. On standing, then warming for a few minutes, cooling, and acidifying with acetic acid, 2-ethylmercapto-5-methyl-6-oxypyrimidine was obtained.

$$
\begin{array}{cc}
NH_2 & C_2H_5OCO \\
| & | \\
C_2H_5SC & CCH_3 \\
\| & \| \\
NH & NaOCH
\end{array}
+
\begin{array}{cc}
NH—CO \\
| \quad | \\
= C_2H_5SC \quad CCH_3 \\
\| \quad \| \\
N——CH
\end{array}
+
\begin{array}{c}
C_2H_5OH \\
\\
NaOH
\end{array}
.
$$
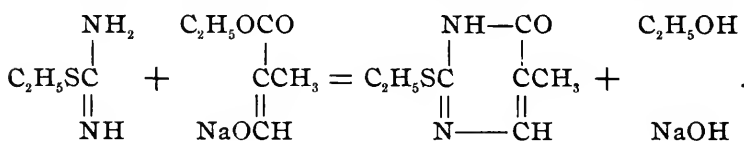
The 2-ethylmercapto-5-methyl-6-oxypyrimidine was converted into 2-ethylmercapto-5-methyl-6-chlorpyrimidine by means of phosphorus pentachloride :

$$
\begin{array}{cc}
NH—CO \\
| \quad | \\
C_2H_5SC \quad CCH_3 \\
\| \quad \| \\
N——CH
\end{array}
+ PCl_5 =
\begin{array}{cc}
N=CCl \\
| \quad | \\
C_2H_5SC \quad CCH_3 \\
\| \quad | \\
N—CH
\end{array}
+ POCl_3. + HCl
$$
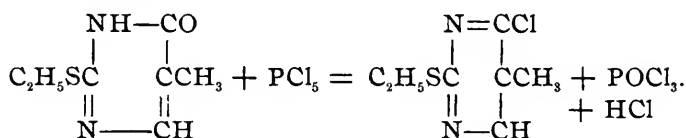
When 2-ethylmercapto-5-methyl-6-chlorpyrimidine was heated with strong alcoholic ammonia it gave 2-ethylmercapto-5-methyl-6-aminopyrimidine.

$$
\begin{array}{cc}
N=CCl \\
| \quad | \\
C_2H_5SC \quad CCH_3 \\
\| \quad \| \\
N—CH
\end{array}
+ 2NH_3 =
\begin{array}{cc}
N=C—NH_2 \\
| \quad | \\
C_2H_5SC \quad CCH_3 \\
\| \quad \| \\
N—CH
\end{array}
+ NH_4Cl.
$$
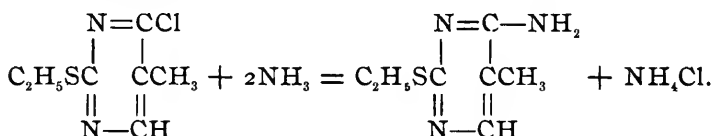
Finally the 2-ethylmercapto-5-methyl-6-aminopyrimidine was converted into the halogen hydride salt of 2-oxy-5-methyl-6-aminopyrimidine by boiling with either hydrochloric or hydrobromic acid.

$$
\begin{array}{cc}
N=C—NH_2 \\
| \quad | \\
C_2H_5SC \quad CCH_3 \\
\| \quad \| \\
N—CH
\end{array}
+ H_2O =
\begin{array}{cc}
N=C—NH_2,HX \\
| \quad | \\
OC \quad CCH_3 \\
| \quad \| \\
HN—CH
\end{array}
+ C_2H_5SH.
$$
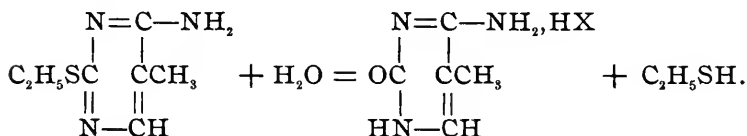
5-Methylcytosine separates from water with a half molecule of water of crystallization while cytosine crystallizes with 1 molecule of water.

5-Methylcytosine is about five times as soluble in water as cytosine and ten or eleven times as soluble as thymine or uracil and it is readily decomposed into thymine by 20 per cent sulphuric acid at 150°. It is probable that in the decomposition of the nucleic acids by the prolonged action of hot acids this base would, if present, be converted entirely into thymine.

One of the most characteristic properties of 5-methylcytosine is its tendency to form the so-called abnormal or basic 2 : 1 salts with hydrochloric and hydrobromic acids. When ammonia in excess is added to a solution of cytosine in these acids, free cytosine usually separates. In the case of 5-methylcytosine in the halogen hydride acids the precipitate generally consists of the salt $(C_5H_7ON_3)_2HX.H_2O$.

Cytosine gives a 1 : 2 salt with concentrated hydrochloric acid; 5-methylcytosine gives a 1 : 1 salt under the same conditions.

The picrate of 5-methylcytosine, which forms yellow, long, slender, needle-like prisms, has the same solubility in water as cytosine picrate.

5-Methylcytosine is precipitated by phosphotungstic acid ; it therefore differs from the new base prepared by Kutscher[1] from thymus nucleic acid.

An attempt was made to prepare 2-oxy-5,6-diaminopyrimidine by brominating 2-ethylmercapto-6-oxypyrimidine[2] (IV.), chlorinating in the 6-position by means of phosphorus pentachloride, and then attempting to replace both of the halogens by the amino group in this compound (VI.) by means of alcoholic ammonia at a high temperature. It was found that the chlorine could be replaced by the amino group with ease, but that the bromine was far more firmly bound, the compound VII. being almost quantitatively obtained. This was converted into 5-bromcytosine (VIII.) and this compound then heated with aqueous ammonia, but here again the desired diamino derivative was not obtained. These results recall the similar behavior of 4-methyl-6-amino-5-brompyrimidine de-

[1] Ztschr. physiol. Chem., **38**, 173 (1903).
[2] Wheeler and Merriam : This JOURNAL, **29**, 484 (1903).

scribed by Gabriel and Colman.[1] This substance did not re-
act with ammonia without complete decomposition.

$$
\begin{array}{ccc}
\underset{\text{IV.}}{\underset{\overset{\displaystyle\parallel\quad\parallel}{\text{N—CH}}}{\text{C}_2\text{H}_5\text{SC}\quad\text{CH}}}\overset{\text{HN—CO}}{}
&
\underset{\text{V.}}{\underset{\overset{\displaystyle\parallel\quad\parallel}{\text{N—CH}}}{\text{C}_2\text{H}_5\text{SC}\quad\text{CBr}}}\overset{\text{HN—CO}}{}
&
\underset{\text{VI.}}{\underset{\overset{\displaystyle\parallel\quad\parallel}{\text{N—CH}}}{\text{C}_2\text{H}_5\text{SC}\quad\text{CBr.}}}\overset{\text{N=CCl}}{}
\end{array}
$$

$$
\begin{array}{ccc}
\underset{\text{VII.}}{\text{C}_2\text{H}_5\text{SC}\quad\text{CBr}} &
\underset{\text{VIII.}}{\text{OC}\quad\text{CBr}} &
\underset{\text{IX.}}{\text{OC}\quad\text{C—NH}_2.}
\end{array}
$$

(IV.) HN—CO / C₂H₅SC CH / N—CH
(V.) HN—CO / C₂H₅SC CBr / N—CH
(VI.) N=CCl / C₂H₅SC CBr / N—CH
(VII.) N=C—NH₂ / C₂H₅SC CBr / N—CH
(VIII.) N=C—NH₂ / OC CBr / HN—CH
(IX.) N=C—NH₂ / OC C—NH₂ / HN—CH
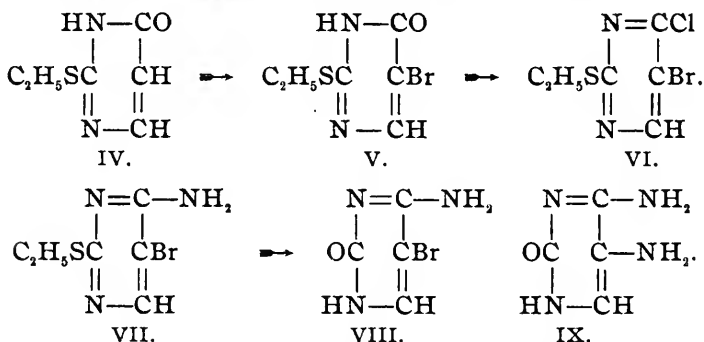
The action of nitric acid was next tried on cytosine, where-
upon it was found that nitration took place ; the compound
formed was not a 5-nitro derivative, but rather the nitramide
whose structure is, in all probability, shown by formula X.

(X.) N=C—NH₂ / OC CH / HN—CH → N=C—NHNO₂ / OC CH / HN—CH
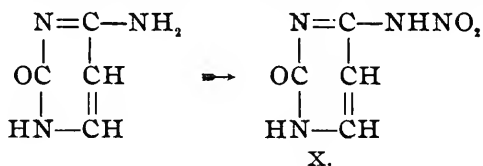
The formation of similar nitramide derivatives in the pyrimi-
dine series has been observed by Gabriel and Colman.[2]

Work on the preparation of oxydiaminopyrimidines will be
continued here. These particular pyrimidine compounds are
of special interest not only because Kutscher[3] believes that
he has isolated such a compound, in the form of its picrate,
from yeast, but also on account of the fact that if an oxydi-
aminopyrimidine is found to crystallize or combine with 3
molecules of water it would then have the same percentage
composition as Drechsel's so-called diaminoacetic acid[4] and
perhaps the substances would prove to be identical. Will-
stätter[5] has shown that diaminoacetic acid, if capable of ex-

[1] Ber. d. chem. Ges., **34,** 1239 (1901).
[2] *Ibid.*, **34,** 1240-1241 (1901).
[3] Ztschr. physiol. Chem., **38,** 176 (1903).
[4] Beilstein : Handbuch I., 1194.
[5] Ber. d. chem. Ges., **35,** 1378 (1902).

istence, would not agree in properties with Drechsel's compound.   In other words, Drechsel's compound might be a pyrimidine derivative as follows :

$$2\left[\begin{matrix} H_2N \\ H_2N \end{matrix} \!\!\!\!> CHCOOH \right] = C_4H_{12}O_4N_4 = C_4H_6ON_4 + 3H_2O.$$
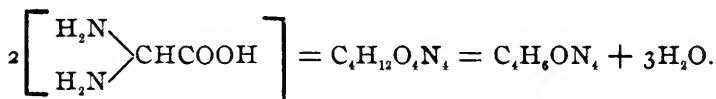
EXPERIMENTAL PART.

2-Ethylmercapto-5-methyl-6-oxypyrimidine,

$$\begin{matrix} HN-CO \\ | \qquad | \\ C_2H_5SC \quad CCH_3. \\ \| \quad \| \\ HN-CH \end{matrix}$$
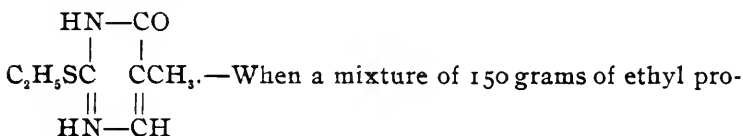
—When a mixture of 150 grams of ethyl pro-
pionate and 135 grams of ethyl formate, in somewhat over 2 volumes of dry ether, were slowly dropped upon 34 grams of sodium, about 125 grams of crude sodium ethylformylpropionate[1] were obtained.   In using this salt and also sodium ethylformyl acetate to condense with the alkyl halide addition-products of thiourea we[2] employed the substances in molecular proportions.   It has since been found in both cases that only about one-half, or less, of the quantity of the salt taken reacts in the desired manner, and therefore that one-half the calculated quantity of pseudoethylthiourea hydrobromide gives about the same, if not a better, yield of pyrimidine as when the substances are used in molecular proportions. From 125 grams of the salt and 150 grams of the ethyl bromide addition-product of thiourea we obtained, in the manner already described, 39.5 grams of this mercaptopyrimidine. This is 28 per cent of the calculated.   In another experiment 90 grams of the sodium salt with 87 grams of the thiourea addition-product gave 20.5 grams of the pyrimidine derivative, or 26 per cent of the theoretical amount.

2-Ethylmercapto-5-methyl-6-oxypyrimidine crystallizes from hot water in the form of long, slender prisms. It is very sol-

[1] Wislicenus : Ber. d. chem. Ges., **20**, 2933 (1887).
[2] This JOURNAL, **29**, 487 ; *Ibid.*, **29**, 496 (1903).

uble in alcohol and it melts at 158° to 159°. A nitrogen determination gave :

	Calculated for $C_7H_{10}ON_2S$.	Found.
N	16.47	16.78

2-Ethylmercapto-5-methyl-6-chlorpyrimidine,

$$\begin{array}{ccc} & N=CCl & \\ & | & | \\ C_2H_5SC & & CCH_3. \\ & \| & \| \\ & N-CH & \end{array}$$

— Phosphorus pentachloride reacts less smoothly with the above mercapto derivative than it does with 2-ethylmercapto-6-oxypyrimidine. When the mixture of the substances in molecular proportions is warmed on the steambath, hydrogen chloride is evolved, and, on cooling, the material solidifies to a deliquescent, crystalline cake. This is apparently a double compound of the chlorpyrimidine and phosphorus oxychloride. If an attempt is made to distil this directly in a vacuum, decomposition takes place and the material turns black. If, however, the cake is transferred to crushed ice it liquefies, and on shaking out with ether and drying, the resulting oil can then be distilled under diminished pressure. In one experiment, 35 grams of the mercapto-oxy derivative and 43.5 grams of phosphorus pentachloride gave 24 grams of the distilled chloride, which is a yield of 61.8 per cent of the calculated. In another, 20 grams gave 14.5 grams of the chloride or 65 per cent of the calculated.

2-Ethylmercapto-5-methyl-6-chlorpyrimidine boils at 146° to 147° at 17 mm. pressure, and at 157° to 159° at 25 to 26 mm. pressure. It was thus obtained as a colorless, almost odorless, oil, which did not solidify in a freezing-mixture.

2-Ethylmercapto-6-chlorpyrimidine, prepared and purified in a similar manner, was found to boil at 135° at 24 mm. pressure.

A nitrogen determination in the case of 2-ethylmercapto-5-methyl-6-chlorpyrimidine, boiling at 157° to 159°, gave :

	Calculated for $C_7H_9N_2SCl$.	Found.
N	14.85	15.00

2-Ethylmercapto-5-methyl-6-aminopyrimidine,
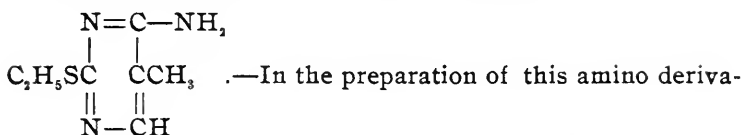
$$\begin{array}{cc} N=C-NH_2 \\ | \quad | \\ C_2H_5SC \quad CCH_3 \\ || \quad || \\ N-CH \end{array}$$.—In the preparation of this amino deriva-

tive, and also in the case of mercaptocytosine, the alcoholic ammonia used should be thoroughly saturated (in the cold), as otherwise an ethoxy derivative is formed instead of an amino compound.

We found that 13 grams of the above chloride and about 75 cc. of alcoholic ammonia, when heated for three hours at 127°, gave 10 grams of amino derivative, or 86.9 per cent of the calculated, and also that 10.1 grams of the chloride, when heated for two hours at 124° to 130°, gave 6.6 grams of the amino base after crystallizing from 50 per cent alcohol, or 74 per cent of the theoretical amount.

2-Ethylmercapto-5-methyl-6-aminopyrimidine is very soluble in alcohol and quite difficultly soluble in water. It crystallizes from 50 per cent alcohol in the form of colorless, small, stout, six-sided tables and prisms, which melt at 96° to 97°. It has a tendency to separate from its solutions as an oil, which finally crystallizes. A nitrogen determination gave :

	Calculated for $C_7H_{11}N_3S$.	Found.
N	24.86	25.20

2-Ethylmercapto-6-ethoxypyrimidine,

$$\begin{array}{cc} N=COC_2H_5 \\ | \quad | \\ C_2H_5SC \quad CH \\ || \quad || \\ N-CH \end{array}$$.—2-Ethylmercapto-6-chlorpyrimidine was
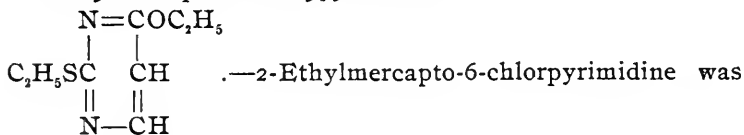
dissolved in alcohol and ammonia gas was passed in, the whole being heated on the steam-bath. After two hours, 7.5 grams of ammonium chloride had separated, the calculated quantity being 7.6 grams. On evaporating the alcoholic solution an oil was obtained which distilled at 137° to 138° at 18 mm.

pressure. A nitrogen determination agreed with the calcula-
ted for an ethoxy derivative :

	Calculated for $C_8H_{12}ON_2S$.	Found.
N	15.21	15.38

That this ethoxy derivative is not an intermediate product
in the preparation of the amino compound was shown when
on heating the oil with alcoholic ammonia for four or five
hours at 150° to 175° it still remained unaltered.

This oil dissolves in dilute hydrochloric acid and is precipi-
tated unaltered by ammonia. On boiling for several hours
with strong acid it is converted quantitatively into uracil,
melting at 338°. A nitrogen determination gave 25.4 per cent
nitrogen, while the calculated is 25.0.

Cytosine Dihydrochloride.—When 2-ethylmercapto-6-amino-
pyrimidine is warmed on the water-bath for three or four hours
with concentrated hydrochloric acid, then cooled, beautiful,
stout, brittle, colorless, flat prisms separate. The following
analysis shows that this material is an acid salt :

	Calculated for $C_4H_5ON_3.2HCl$.	Found.
Cl	38.58	39.09

This salt is analogous to the acid sulphate, $C_4H_5ON_3.$
H_2SO_4, described by Kossel and Steudel.[1]

5-Methylcytosine Monohydrochloride (Anhydrous).—When
2-ethylmercapto-5-methyl-6-aminopyrimidine was warmed
with hydrochloric acid, in a similar manner to the above,
mercaptan was evolved and the crystals obtained were color-
less tables and flat prisms, which, when dried over potassium
hydroxide, showed signs of melting at about 270°, and melted
with effervescence at 288°. The material was readily soluble
in water. A chlorine determination showed that this was an
anhydrous 1 : 1 salt.

	Calculated for $C_5H_7ON_3.HCl$.	Found.
Cl	21.98	21.99

When 6.6 grams of the crude mercapto base were warmed

[1] Ztschr. physiol. Chem., **38**, 53 (1903).

on the steam-bath with hydrochloric acid until mercaptan ceased being evolved, the solution evaporated to dryness, and the residue dissolved in a little water, 0.7 gram thymine was obtained, the formation of this being due to the presence of an ethoxy derivative. When this 1 : 1 hydrochloride was dissolved in water and to the warm solution an excess of ammonia was added, microscopic colorless needles slowly separated. These were not very soluble in hot water and difficultly in cold. The material was recrystallized from water. The curious result was then observed that the material still contained chlorine and that we had to deal with a basic salt or, more probably, a mixture of free base and a hydrous basic salt. The analytical results agreed fairly with the calculated for $(C_5H_7ON_3)_22HCl.3H_2O$.

	Calculated.	Found.
Cl	9.4	9.09
H_2O	7.1	7.53

The water determination was made by heating the material to constant weight at 150°. When the 1 : 1 hydrochloride is boiled with water a basic salt also is obtained.

$$N=C-NH_2$$
$$\quad\quad\mid\quad\quad\mid$$
5-Methylcytosine, $OC\quad CCH_3$.—In order to obtain the
$$\quad\quad\mid\quad\quad\parallel$$
$$HN-CH$$
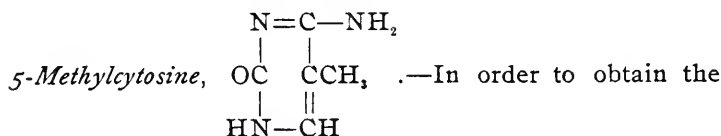
free base the above material was dissolved in water, the chlorine was removed by means of silver sulphate, the excess of silver was precipitated with hydrogen sulphide and the sulphuric acid by barium hydrate, the excess of the latter by carbon dioxide. The clear, colorless solution was then concentrated to a small volume, whereupon, on cooling, beautiful, flat, colorless, prismatic, brittle crystals separated that formed a sandy powder. When heated, the crystals gave off water above 100° and showed signs of melting at 240°, melting with effervescence at 270°; this is 50° lower than the melting-point of cytosine.

100 parts of water dissolved 4.5 parts of the base at 25°.

2.387 gram substance lost 0.1544 gram on heating to constant weight at 135° to 145° (I.).

	Calculated for $(C_5H_7ON_3)_2.H_2O$.	Found. I.	II.
H_2O	6.71	6.46	6.30

	Calculated for $C_5H_7ON_3$.	Found.
N	33.60	33.44

Silver nitrate, added to an aqueous solution of this base, gives a gelatinous white precipitate soluble in an excess of ammonia and in nitric acid. The ammonia solution can be boiled without reduction.

Mercuric chloride gives a white precipitate in dilute solutions of the base; this dissolves on heating and separates again, on cooling, possibly in crystalline form.

Phosphotungstic acid gives a white precipitate insoluble in dilute hydrochloric or sulphuric acids.

5-Methylcytosine Monohydrochloride (*Hydrous*).—An attempt was made to prepare a dihydrochloride of the methyl base by dissolving the above 1 : 1 salt in water and then saturating the solution with hydrogen chloride. The solution was then allowed to evaporate spontaneously in a desiccator over sulphuric acid, whereupon small, stout, transparent prisms or rhombohedrons separated. The analysis agreed with the calculated for the formula $C_5H_7ON_3.HCl.2H_2O$.

	Calculated.	Found.
H_2O	18.2	18.0
Cl	21.98	22.0

On keeping these crystals in a closed tube they became opaque.

5-Methylcytosine Basic Hydrochloride.—Experiments were made to determine whether or not 5-methylcytosine gives a 2 : 1 and a 3 : 1 salt by mixing solutions of the base and the above hydrochloride in the required proportions. It was found that when a strong solution of the base (0.12 gram) was mixed with a warm solution of the hydrochloride (0.153 gram) in a little water a precipitate was formed immediately. This dissolved on boiling, and on cooling, little balls of mi-

nute needles or prisms separated. When dried over calcium chloride the salt was found to have the composition represented by Analysis I. When two molecular proportions of the base to one of the hydrous hydrochloride were used the same basic salt was obtained. For example : 0.15 gram of the hydrochloride was dissolved in 2.5 cc. of water and 2.2 grams of the base were dissolved in 5 cc. of water. On mixing these solutions at ordinary temperature a gelatinous mass separated, so bulky that the test-tube could be inverted without loss of the contents. On warming, the material dissolved and on cooling small prisms separated. Analysis II.:

	Calculated for $(C_5H_7ON_3)_2HCl.H_2O$.	I.	Found. II.
H_2O	5.9	6.2	5.9
Cl	11.6	11.3	

This hydrous basic salt is analogous to the hydrous basic cytosine sulphate frequently obtained by Levene.[1] This salt has the formula $(C_4H_5ON_3)_4H_2SO_4.2H_2O$.

The corresponding anhydrous basic sulphate has been described by Kossel and Steudel.[2]

A neutral sulphate of cytosine has also been described by Levene.[3]

5-Methylcytosine Basic Hydrobromide.—Ten grams of 2-ethyl-mercapto-5-methyl-6-aminopyrimidine were boiled with 15 cc. of strong hydrobromic acid for four hours. The acid was then evaporated, whereupon beautiful, large, stout prisms separated. These crystals were very soluble in water. Upon adding strong ammonia to the warm aqueous solution an immediate precipitate in the form of a fine, crystalline powder was obtained. The yield was 7 grams. This precipitate was difficultly soluble in water. When heated it sintered at about 295° and then decomposed with effervescence at 319°–320°. This material was boiled for some time with strong aqueous ammonia ; it nevertheless still contained bromine, and on analysis the following results were obtained : The air-dried salt lost water very slowly below 150°, dried at 175°–185°.

[1] Ztschr. physiol. Chem., **39**, 7 ; **39**, 135, 481 (1903).
[2] *Ibid.*, **38**, 53 (1903).
[3] *Ibid.*, **37**, 405 (1903).

0.4838 gram lost 0.0290 gram water or 5.9 per cent. The calculated for $(C_5H_7ON_3)_2HBr.H_2O$ is 5.1 per cent. The dried residue then gave the following results :

	Calculated for $(C_5H_7ON_3)_2HBr$.	Found.
C	36.25	36.20
H	4.53	4.85
N	25.37	25.68

This basic salt was then treated with silver sulphate as described above in the case of the basic hydrochloride. The free base obtained agreed in every particular with the preparation from the basic hydrochloride. A water determination is given above (II.).

When 0.7 gram of this basic salt was heated at 150°–160° for three hours with 20 per cent sulphuric acid, 0.20 gram of thymine, melting at 325°–326°, was obtained. Forty per cent of the material was therefore hydrolyzed.

Acetyl-5-methylcytosine, prepared by dissolving the base in acetic anhydride, forms needles from water. The material did not melt or effervesce below 290° although it showed signs of decomposition at about 255°.

5-Methylcytosine Picrate.—When 0.238 gram of the base in a little water was mixed with 40 cc. of a saturated aqueous solution of picric acid, an immediate precipitate was formed. This dissolved on boiling and adding more water; on cooling, long, slender, bright yellow, needle-like prisms separated. On heating, this material showed signs of change at about 250°–255° and from then on got darker until at 286° it decomposed with effervescence. A certain mixture of this material with pure cytosine picrate began to change color, on heating, at 255° and melted with effervescence at 273°. It is noteworthy that this picrate has the same solubility in water as cytosine picrate.[1] One hundred parts of water dissolve 0.07 part of the salt.

The *chloroplatinate* is quite soluble in water. The aqueous solution, on standing in a desiccator, deposits small orange-colored rosettes.

[1] Wheeler and Johnson : *Loc. cit.*

2-Ethylmercapto-5-brom-6-oxypyrimidine,

$$\begin{array}{c} \text{HN---CO} \\ | \qquad | \\ \text{C}_2\text{H}_5\text{SC} \quad \text{CBr.} \\ || \quad || \\ \text{N---CH} \end{array}$$ —— When 2-ethylmercapto-6-oxypyrimidine
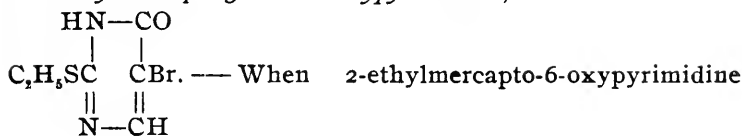
(5.55 grams) was dissolved in three parts of glacial acetic acid and one molecular proportion of bromine was added (6 grams), a mass of needles separated; these were washed with water and dried; the weight was 7.45 grams or 89 per cent of the calculated. In another experiment 16 grams of the mercapto compound gave 22.1 grams of the brom-derivative or 91.7 per cent of the theoretical amount. This material was difficultly soluble in water, but more readily soluble in alcohol, from which solution beautiful, colorless, needle-like prisms were obtained. These, on heating, showed signs of change at about 184° and melted completely without effervescence at 189°. A nitrogen determination gave:

	Calculated for $C_6H_7ON_2SBr$.	Found.
N	11.9	12.1

An excess of bromine does not effect further substitution in the cold. When the substance is boiled with hydrochloric acid, 5-bromuracil is obtained.[1] Dr. Merriam found that when this latter substance was heated with aqueous ammonia to 180°, 5-aminouracil resulted, the compound being identified by means of its picrate.[2]

The action of alcoholic ammonia on the brommercapto compound at temperatures between 140° and 200° did not lead to a smooth result.

2-Ethylmercapto-5-brom-6-chlorpyrimidine,

$$\begin{array}{c} \text{N===CCl} \\ | \qquad | \\ \text{C}_2\text{H}_5\text{SC} \quad \text{CBr.} \\ || \quad || \\ \text{N---CH} \end{array}$$ —2-Ethylmercapto-5-brom-6-oxypyrimidine
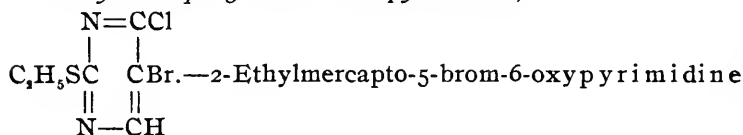
(21 grams) and phosphorus pentachloride (18.6 grams) were mixed and warmed on the steam-bath. After standing over

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[1] Wheeler and Merriam : *Loc. cit.*
[2] Behrend and Grünwald : Ann. Chem. (Liebig), **309**, 258 (1899).

night the phosphorus oxychloride was removed by distilling under diminished pressure and the remaining oil poured off from a small amount of resin ; this was washed with a little ether. The weight of crude oil then obtained, on evaporating the ether, was 20.5 grams or 92 per cent of the calculated. On standing, this oil solidified in the form of soft, talc-like, colorless plates which, when pressed on paper, melted at about 27°. A nitrogen determination then gave :

	Calculated for $C_6H_6N_2SClBr.$	Found.
N	11.04	11.06

2-Ethylmercapto-5-brom-6-aminopyrimidine,

$$
\begin{array}{ll}
\text{N=C—NH}_2 \\
\quad| \quad | \\
\text{C}_2\text{H}_5\text{SC} \quad \text{CBr} \\
\quad\| \quad \| \\
\text{N—CH}
\end{array}
$$
.—The above chlorobromide (19 grams)
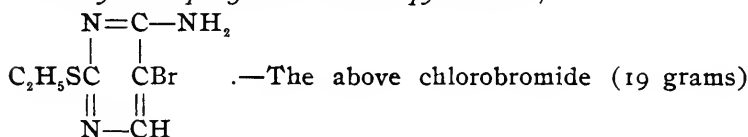
was heated with alcoholic ammonia (40 cc. cold saturated solution) to 160° for four hours. On cooling, a crystalline mass separated with little or no color. Water was added to the contents of the tube ; the material that separated, on drying, weighed 15.7 grams or 89.7 per cent of the calculated. The substance was readily soluble in hot alcohol and difficultly in cold, and very difficultly soluble in hot water. On crystallizing from alcohol it formed beautiful, colorless prisms which melted sharply at 123° to 124°. The material contained sulphur and bromine, and a nitrogen determination gave the following result :

	Calculated for $C_6H_8N_3SBr.$	Found.
N	17.9	17.8

5-Bromcytosine,

$$
\begin{array}{ll}
\text{N=C—NH}_2 \\
\quad| \quad | \\
\text{OC} \quad \text{CBr} \\
\quad| \quad \| \\
\text{HN—CH}
\end{array}
$$
. — Twelve grams of the
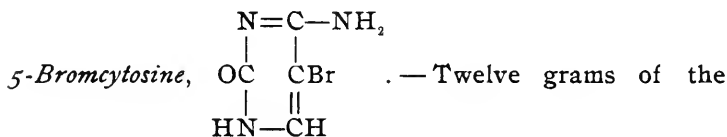
above mercapto compound were boiled with 50 cc. of concentrated hydrochloric acid for four or five hours. The acid was then evaporated and the residue crystallized from water,

whereupon minute prisms of the hydrochloric acid salt were obtained. To the hot solution of this material strong ammonia was added in excess, and then, on cooling, bunches of needle-like prisms of the free base separated. The yield was 7.5 grams, or 77.3 per cent of the calculated, more being obtained from the mother-liquor. When the pure base, crystallized from water, was heated it gave no definite melting-point but decomposed rapidly above 235°. A nitrogen determination gave :

	Calculated for $C_4H_4ON_3Br$.	Found.
N	22.10	22.11

When this material was heated at 155° to 190° with concentrated aqueous ammonia for four hours, the products were a black resin and a brick-red amorphous powder, the material having undergone decomposition.

$$N=C-NH-NO_2$$

Nitrocytosine, OC CH .—Two grams of anhy-

$$HN-CH$$
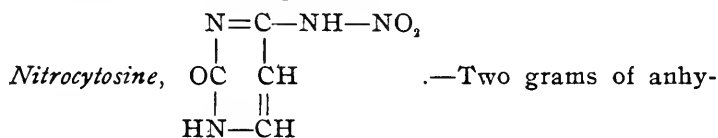
drous cytosine (synthetic), 4. cc. of concentrated nitric acid, and 4 cc. of concentrated sulphuric acid were mixed and warmed for a few minutes at 85°. The mixture was then poured upon crushed ice and neutralized (slight excess of ammonia added). The crystalline material that separated weighed 1.8 grams, or 64 per cent of the calculated. In another experiment 2 grams of cytosine and 6 cc. of each acid gave 1.7 grams of the crude nitro compound. This nitro compound is very difficultly soluble in water, from which it separates in the form of colorless, minute needles. These are readily soluble in strong ammonia. When heated, the material begins to turn brown at about 280°, decomposes rapidly above 300°, but does not melt or effervesce at 350°. A nitrogen determination gave the following result :

	Calculated for $C_4H_4O_3N_4$.	Found.
N	35.89	35.80

When an attempt was made to reduce this material with

tin and hydrochloric acid the only crystalline material obtained was ammonium chloride. According to Behrend and Grünwald[1] 5-nitrouracil gives 80 per cent of the calculated of aminouracil, when reduced in ammoniacal solution by means of aluminium amalgam. An attempt to reduce our nitrocytosine in a similar manner gave nothing but amorphous yellow and blue-black decomposition-products. For this reason the above nitramide structure is assigned to the compound.

NEW HAVEN, CONN., Feb. 1, 1904.

ON THE REDUCTION OF NITRATES BY CERTAIN PLANT EXTRACTS AND METALS AND THE ACCELERATING EFFECT OF CERTAIN SUBSTANCES ON THE PROGRESS OF THE REDUCTION.

BY J. H. KASTLE AND ELIAS ELVOVE.[2]

The fact that both higher and lower plants are able to construct proteids out of nitrates naturally suggests that the nitrates must suffer a gradual reduction in this phase of nitrogen metabolism. It has been observed that certain plants, such as the tobacco, contain so much nitrate in their leaves that this crystallizes out on drying, and the writers of this communication have obtained excellent tests for nitrite on several specimens of air-dried tobacco. Whether this nitrite is of bacterial origin or results from reducing changes naturally occurring in the leaf itself we have not yet been able to determine. Indeed, chemists seem to be divided in opinion as to whether nitrites ever occur in the living plant. According to Molisch,[3] for example, nitrites could not be detected in one hundred different plants which he examined. According to this observer all statements as to the presence of nitrites in plants are based on experimental errors and incorrect interpretation of results. According to him plants possess the power of reducing nitrites with surprising rapidity, whereas nitrates will remain for weeks, and even months, in vegetable cells before

they are destroyed. On the other hand, Modderman[1] was able to detect nitrites in the exudations of the fuchsia, by means of starch, potassium iodide, and sulphuric acid, and also by means of other reagents. Recently also K. Aso[2] has called attention to the occurrence of nitrites in the buds of the potato and *Sagittaria sagittæfolia*. In view of these facts it seemed of interest to determine whether the aqueous extracts of certain plants had the power of reducing nitrates to nitrites. In other words, this investigation had for its object to determine whether any of the higher plants can bring about those changes ordinarily included under the head of denitrification.

According to Berthelot,[3] in the leaves and all such organs of the plant, the conditions which tend to the production of nitrates by oxidation of nitrogenous substances and those which tend toward the reduction of nitrates, result ultimately in a state of unstable equilibrium (*equilibre mobile*) with respect to the assimilation of nitrogen. The agents which produce such results being, on the one hand, those which bring about reduction, and on the other, those which effect oxidation in the living organism, that is to say, they thus resemble the soluble ferments, or more generally oxidizable principles, which by their oxidation can effect the oxidation of other substances. The existence of such a substance in the potato was long ago pointed out by Schönbein and confirmed by Kastle and Loevenhart.[4] That is to say, the potato contains easily oxidizable substances, which on exposure to the air are converted into oxidases by processes of autoxidation. It therefore occurred to us that the potato would probably prove to be a convenient plant material with which to begin the investigation.

Preparation and Denitrifying Properties of the Aqueous Extract of the Potato Tuber.

The aqueous extract of the potato was usually prepared by

[1] Ann. Agronom., **14**, 423–424.
[2] Bull. Agric. Coll., Tokyo Imp. Univ., **5**, 487.
[3] Berthelot : Chimie Vegetale et Agricole, **3**, 183, 469, 507.
[4] This JOURNAL, **26**, 539–566.

cutting up the inner portion of a potato tuber into small pieces and macerating rapidly in a mortar with 100 to 150 cc. of water. Generally the extract thus obtained was not filtered, but simply decanted off from the larger pieces and immediately used in the experiment, for the reason that filtration seemed to diminish the activity of the extract, and also because this would result in a longer exposure to the air, and this likewise seems to diminish its denitrifying powers. An extract which was allowed to stand for two days under antiseptic conditions was found at the end of that time to have completely lost its activity. In most cases 10 cc. of the fresh extract were employed. To this was added 0.5 cc. of toluene as antiseptic, and finally, 2 cc. of a solution of pure sodium, potassium, or ammonium nitrate of known concentration. The tube containing the mixture was then tightly corked and shaken, and allowed to stand at a certain temperature, usually 40° C., for the desired interval, at the end of which time 2 cc. were pipetted out and tested for nitrite with Griess' sulphanilic acid reagent, and the amount of nitrite, if found present, determined colorimetrically. Control experiments were tried in all cases. In these the same aqueous extract was employed as that used in any particular series of experiments, the only difference being that in the control experiments the extract was boiled before the addition of the nitrate. The effect of temperature, of various antiseptics, of varying the concentration of nitrate and potato extract, on the progress of the reaction, have all been investigated. The results of our studies are given in the following pages.

The fact that an aqueous extract of the potato tuber can reduce a nitrate to a nitrite is apparent from the results reached in the following experiments :

Experiment 1.—A fresh potato extract was prepared. Two tubes received 10 cc. each of the non-filtered extract. To one of these was immediately added 0.5 cc. of toluene, while the other was heated to boiling for three minutes. It was then cooled, diluted with water to the original volume, and 0.5 cc. of toluene added to it also. To each tube there was then added simultaneously 5 cc. of a solution of pure sodium

nitrate containing 0.5 gram of the salt. Both tubes were then tightly corked and shaken, and allowed to remain at 40° C. for two hours. At the end of this time 2 cc. were pipetted out from each tube and tested for nitrite. The following results were obtained :

Two cc. of the active liquid contained nitrite equal to 0.120 cc. of the standard,[1] or a total of 0.16407 milligram.

Two cc. of the boiled liquid contained no nitrite.

Experiment 2.—This was similar in every respect to the above, except that the 5 cc. of sodium nitrate solution added to each tube contained only 0.025 gram of the salt. After allowing both tubes to remain at 40° C. for two hours the following results were obtained :

Two cc. of the active liquid contained nitrite equal to 0.100 cc. of the standard, or a total of 0.13673 milligram.

Two cc. of the boiled liquid contained no nitrite.

Experiment 3.—This was similar in every respect to Experiment 1, except that the amount of antiseptic added to each tube was increased to 1 cc. After standing for two hours at 40° C. the following results were obtained :

Two cc. of the active liquid contained nitrite equal to 0.085 cc. of the standard, or a total of 0.11622 milligram.

Two cc. of the boiled liquid contained no nitrite.

Experiment 4.—This differed from Experiment 1 only in that the extract was quickly filtered once. After two hours' standing at 40° C. the following results were obtained :

Two cc. of the active liquid contained nitrite equal to 0.075 cc. of the standard, or a total of 0.10254 milligram.

Two cc. of the boiled liquid contained no nitrite.

It should be noted in this connection that our earlier work along this line led invariably to negative results. It was found out afterwards, however, that the failure was due partly to the fact that the nitrate solution employed was too dilute. It became of interest, therefore, to determine the effect of varying the amount of nitrate on the progress of the reduction. The experimental data and results obtained are given in Table I.

[1] One cc. of the standard employed contained 0.18231 milligram of sodium nitrite.

Table I.

The indicated amount of sodium nitrate was added to 20 cc. of fresh potato extract containing 0.5 cc. of toluene as antiseptic.

Time, three hours.   Temperature, 30° C.

No. of experiment.	Amount of sodium nitrate in grams.	Nitrite in 2 cc. expressed in cc. of standard.	Total nitrite expressed in cc. of standard.	Amount of nitrite in milligrams.
1	0.001	0.080	0.800	0.14584
2	0.010	0.100	1.000	0.18231
3	0.050	0.145	1.450	0.26434
4	0.250	0.200	2.000	0.36462
5	1.250	0.290	2.900	0.52869
6	6.250	0.340	3.400	0.61985
7	10.000	0.200	2.000	0.36462

It will be seen from an examination of the results given in Table I. that the amount of nitrite formed in three hours at 30° C. by the action of 20 cc. of the aqueous extract of the potato on sodium nitrate increases, more or less regularly, with increasing amounts of nitrate until a maximum is reached with 6.25 grams of sodium nitrate, the amount of nitrite formed being more than when 10 grams of the salt are used. Hence the effect of increasing the amount of nitrate is to increase the amount of nitrite formed, so long as the amount used is below a certain maximum, after which the effect is to retard the reduction. This is probably to be explained by the poisonous action of the salt at greater concentration.

The Effect of Temperature on the Reduction of Sodium Nitrate by Aqueous Extracts of the Potato.

The effect of temperature on the progress of the reaction under investigation has also been studied. The experimental data and results are given in Table II. :

Table II.

Ten cc. of potato extract containing 0.5 cc. of toluene as antiseptic, 5 cc. of a sodium nitrate solution containing 0.5 gram of the salt.

Time, two and one-half hours.

No. of experiment.	Temperature.	Nitrite in 2 cc. expressed in cc. of standard.	Total nitrite expressed in cc. of standard.	Amount of nitrite in milligrams.
1	0°– 5° C.	0.002	0.015	0.00273
2	10°–15° C.	0.005	0.037	0.00674
3	15°–20° C.	0.010	0.075	0.01367
4	30° (room temp.)	0.100	0.750	0.13673
5	40°–45° C.	0.130	0.975	0.17775
6	45°–50° C.	0.100	0.750	0.13673
7	50°–55° C.	0.060	0.450	0.08203
8	55°–60° C.	0.055	0.412	0.07511
9	60°–70° C.	0.050	0.375	0.06836
10	75°–80° C.	0.001	0.007	0.00127
11	100° C.	0.000	0.000	0.00000

It will be observed that the amount of nitrite formed increases with rise of temperature, reaching a maximum at 40° to 45° C., above which it begins to decrease in amount, becoming nil at 100° C. The optimum temperature of the reaction is, therefore, between 40° and 45° C. We thus see that the change under investigation is similar to other biochemic and zymotic processes, so far as the influence of temperature is concerned.

The Effect of Increasing Amounts of the Potato Extract on the Reduction.

The effect of increasing the quantity of the potato extract on the reduction here under investigation has also been tried. The conditions and results of these experiments are given in Table III. :

Table III.

Number of cubic centimeters of potato extract varying as indicated in column 2 of table ; 2 cc. of 50 per cent solution of sodium nitrate ; 0.5 cc. of toluene as antiseptic ; the whole made up to 28 cc. with distilled water.

Time, twelve hours.   Temperature, 30° C.

No. of experiment.	Potato extract in cc.	Nitrite in 2 cc. expressed in cc. of standard.	Total nitrite expressed in cc. of standard.	Amount of nitrite in milligrams.
1	5	0.050	0.700	0.12761
2	10	0.090	1.260	0.22971
3	15	0.120	1.680	0.30628
4	20	0.140	1.960	0.35733
5	25	0.150	2.100	0.38286

It will be observed that the amount of nitrite formed increases with the amount of the potato extract present. With small amounts of the extract, as will be observed from Experiments 1 and 2, the amount of nitrite formed is nearly exactly proportional to the quantity of extract employed. Thus the amount of nitrite formed in Experiment 2 was 0.22971 milligram, whereas if the amount formed were exactly proportional to the amount of extract used, it should have been 0.25522 milligram. On the other hand, the amount of nitrite formed when 25 cc. of the potato extract was employed was only 0.38286 milligram, whereas, had it been exactly proportional to the quantity of the extract employed it should have been 0.63805 milligram. Hence the reduction by increasing quantities of the reducing substance in the potato tends toward a maximum, which is probably not further augmented by increasing amounts of the potato extract. The same is true of the action of certain, if not all, of the soluble ferments.

On the Inhibiting Action of Certain Substances on the Reduction of Nitrates by the Potato Extract.

It is known that most biochemical processes and zymotic changes are inhibited, and often completely checked, by the

presence of certain poisons. It therefore occurred to us to try the effect of certain poisonous substances on the change under investigation. The names of the substances tried, together with the quantities employed, and the other conditions of the experiments, as well as the results, are given in Table IV. :

Corresponding controls showed no nitrite. It was also ascertained that none of the substances mentioned in the above table interfere with the nitrite test when present in the proportions used in the above experiments. It is evident from these results that the reduction of nitrates by the aqueous extracts of the potato is completely inhibited or checked by mercuric chloride, chloroform, resorcinol, and also by alkalies. Its activity is also greatly lessened by phenol, phenylhydrazine hydrochloride, sodium hypophosphite, hydroquinone, hydroxylamine hydrochloride, benzenesulphinic acid, sodium fluoride, and hydrocyanic acid.

Accelerating Effect of Certain Substances on the Progress of the Reduction.

In order to exclude denitrifying organisms we were careful in our earlier work to use considerable amounts of toluene as antiseptic. On comparing the activity of a certain extract alone and in the presence of toluene, it was observed that the toluene apparently accelerated the reduction, that is, more nitrite was formed in the presence than in the absence of this substance, and yet toluene alone has no power to reduce a nitrate, under the conditions of our experiments. This led us to study the effect of a large number of substances on the progress of the reaction. The name of the substance tested, and the amount of it employed, together with the general conditions of the experiments and the results obtained, are given in Table V.

Corresponding controls showed no nitrite.

It will be observed that quite a considerable number of substances, notably alcohols and aldehydes, have the power of greatly accelerating the reduction of sodium nitrate by potato extract. The accelerating action of benzyl alcohol and benzaldehyde especially is very remarkable. By comparing

Table IV.

Ten cc. potato extract; 2 cc. of a 50 per cent. solution of sodium nitrate; 5 cc. water, or solution containing the indicated amount of the substance.

Time, one hour.						Temperature, 40° C.

Substance.	Amount of substance used.	Nitrite in 2 cc. expressed in cc. of standard.	Total nitrite expressed in cc. of standard.	Amount of nitrite in milligrams.
None		0.030	0.255	0.04649
Hydrocyanic acid	0.1 cc. N/10 solution	0.025	0.212	0.03865
" "	0.5 cc. N/10 "	0.018	0.153	0.02789
Sodium fluoride	1 part NaF : 1000 parts liquid	0.015	0.127	0.02315
"	1 part NaF : 500 parts liquid	0.010	0.085	0.01550
Hydrocyanic acid	1 cc. N/10 solution	0.010	0.085	0.01550
Benzenesulphinic acid	1 cc. 1 per cent solution	0.010	0.085	0.01550
Hydroxylamine hydrochloride	1 part : 1000 parts liquid	0.005	0.042	0.00766
Hydroquinone	0.1 gram	0.005	0.042	0.00766
Sodium hypophosphite	1 cc. 20 per cent solution	0.003	0.025	0.00456
Phenylhydrazine hydrochloride	5 cc. N/100 solution	0.002	0.017	0.00310
Phenol	0.1 cc.	0.002	0.017	0.00310
Resorcinol	0.1 gram	0.000	0.000	0.00000
Chloroform	0.5 cc.	0.000	0.000	0.00000
Mercuric chloride	1 part : 1000 parts liquid	0.000	0.000	0.00000
Lime-water	Sufficient to neutralize acidity	0.000	0.000	0.00000
Sodium hydroxide	1 cc. N/10 solution	0.000	0.000	0.00000

Table V.

Ten cc. potato extract; 2 cc. 50 per cent solution of sodium nitrate; 1 cc. water, or solution containing the indicated amount of accelerator.

Temperature, 40° C.

Time, one hour.

Accelerator.	Amount of accelerator.	Nitrite in 2 cc. expressed in cc. of standard.	Total nitrite expressed in cc. of standard.	Amount of nitrite in milligr'ms.
None		0.025	0.1625	0.02962
Methyl alcohol	0.05 cc.	0.030	0.1950	0.03555
Acetone	0.1 "	0.040	0.2600	0.04740
Bromal	0.1 gram	0.045	0.2925	0.05332
Chloral	0.1 "	0.050	0.3250	0.05925
Eugenol	0.1 cc.	0.050	0.3250	0.05925
Propyl alcohol	0.1 "	0.065	0.4225	0.07702
Formaldehyde	1 cc. of 4 per cent solution	0.075	0.4875	0.08887
Salicylic aldehyde	0.1 cc.	0.075	0.4875	0.08887
Glucose	0.1 gram	0.080	0.5200	0.09480
Allyl alcohol	0.1 cc.	0.085	0.5525	0.10072
Toluene	0.5 "	0.090	0.5850	0.10665
Ethyl alcohol	1 cc. 90 per cent	0.090	0.5850	0.10665
Thymol	0.5 cc. 10 per cent alcoholic solution	0.090	0.5850	0.10665
o-Nitrobenzaldehyde	0.1 gram	0.090	0.5850	0.10665
Levulose	0.1 cc.	0.120	0.7800	0.14220
Vanillin	0.1 gram	0.180	1.1700	0.21330
Acetaldehyde	1 cc. 4 per cent solution	0.600	3.9000	0.71100
Benzaldehyde	0.1 cc.	0.650	4.2250	0.77025
Benzyl alcohol	0.1 "			

the quantities of nitrite produced when 0.1 cc. of these substances were present with that formed by the potato extract alone, it will be seen that each of these substances has increased the amount of nitrite formed from twenty-five to thirty times. The fact, too, that many of these accelerators are poisonous and antiseptic in their general properties enhances the interest attaching to their action on the change under consideration, and the further fact that the control experiments differing only from the other experiments in that the extract of the potato had been boiled previous to use, gave no test for nitrite shows that these various accelerators alone have not the power to reduce nitrates, under the conditions here employed. The further significance of these results will be discussed in a subsequent part of this communication.

On the Effect of Temperature on the Reduction of Nitrates by the Potato Extract, in the Presence of an Accelerator.

The effect of the accelerator on the reduction of nitrates by the potato extract has been studied under a variety of conditions. Among other things, the effect of temperature on the reduction in the presence of an accelerator has been investigated, using formaldehyde, acetic aldehyde, benzaldehyde, ethyl and benzyl alcohols as accelerators. The general conditions of the experiments, together with the results obtained, are given in Table VI. :

A comparison of the results in Table VI. with those given in Table II. goes to show that the effect of temperature on the reduction is essentially the same, both in the presence and absence of an accelerator. The optimum temperature of the reduction in the absence of an accelerator was found to be between 40° and 45° C., and in the presence of benzyl and ethyl alcohol and acetic and benzoic aldehydes the optimum temperature of the reaction was also found to be 40° C., whereas in the presence of formic aldehyde it was found that the largest amount of nitrite was formed at 60° C. The fact that very small amounts of nitrite were produced even at 100° C., in the presence of certain of these accelerators, is doubtless to be explained on the ground that at these higher tem-

Table VI.

10 cc. potato extract; 2 cc. 35 per cent solution of potassium nitrate; 1 cc. water, or solution containing the indicated amount of accelerator.

Time, one hour.

Temperature, C.	Accelerator.	Amount of accelerator.	Nitrite in 2 cc expressed in cc. of standard.	Total nitrite expressed in cc. of standard.	Amount of nitrite in milligrams.
0	Formaldehyde	1 cc. N/5 solution	0.040	0.260	0.05826
20	"	1 " N/5 "	0.085	0.552	0.12370
40	"	1 " N/5 "	0.120	0.780	0.17480
60	"	1 " N/5 "	0.150	0.975	0.21850
80	"	1 " N/5 "	0.010	0.065	0.01457
100	"	1 " N/5 "	0.005	0.032	0.00727
0	Acetaldehyde	1 cc. 1 per cent solution	0.080	0.520	0.11653
20	"	1 " 1 " "	0.220	1.430	0.32046
40	"	1 " 1 " "	0.240	1.560	0.34960
60	"	1 " 1 " "	0.125	0.812	0.18197
80	"	1 " 1 " "	0.025	0.162	0.03630
100	"	1 " 1 " "	0.015	0.097	0.02174
0	Benzaldehyde	0.1 cc.	0.060	0.390	0.08740
20	"	0.1 "	0.220	1.430	0.32046
40	"	0.1 "	0.650	4.225	0.94682
60	"	0.1 "	0.090	0.585	0.13110
80	"	0.1 "	0.000	0.000	0.00000
100	"	0.1 "	0.000	0.000	0.00000

Table VI. (Continued).

Tempera-ture C.	Accelerator.	Amount of accelerator.	Nitrite in 2 cc. expressed in cc. of standard.	Total nitrite expressed in cc. of standard.	Amount of nitrite in milligrams.
0	Ethyl alcohol	1 cc. 90 per cent solution	0.060	0.390	0.08796
20	"	1 " 90 "	0.100	0.650	0.14494
40	"	1 " 90 "	0.110	0.715	0.16015
60	"	1 " 90 "	0.050	0.325	0.07276
80	"	1 " 90 "	0.015	0.097	0.02174
100	"	1 " 90 "	0.005	0.032	0.00717
0	Benzyl alcohol	0.1 cc.	0.095	0.617	0.13827
20	"	0.1 "	0.225	1.462	0.32763
40	"	0.1 "	0.675	4.387	0.98312
60	"	0.1 "	0.210	1.365	0.30590
80	"	0.1 "	0.085	0.552	0.12370
100	"	0.1 "	0.020	0.130	0.02914

Note.—Control experiments with each of the above accelerators, in which the boiled extract was employed instead of the active, were kept at the optimum temperature, without showing more than mere traces of nitrite.

peratures the accelerators themselves are rendered sufficiently active to reduce a very minute quantity of the nitrate.

Effect of Time on the Reduction of the Nitrate by the Potato Extract in the Presence of an Accelerator.

The effect of time on the reduction of the nitrate by the potato extract in the presence of certain accelerators has also been studied. The results obtained, together with all necessary data, are given in Table VII.

Control experiments with each of the accelerators employed above, gave none or only slight traces of nitrite.

It will be observed that the longer the substances are allowed to remain together the more nitrite is produced. However, the quantity of nitrite formed is not proportional to the time interval of the reaction. Proportionately a much larger quantity of nitrite is formed during the first hour than during either the second or the third. It is interesting to note, however, that in most cases the quantity of nitrite formed during the first two hours is almost an exact mean between that formed in one and three hours. This affords a convenient check on the results.

On the Effect of Increasing Amounts of Nitrate on the Reduction by Potato Extract in the Presence of Certain Accelerators.

The effect of increasing amounts of nitrate on the reduction of nitrate by the potato extract in the presence of formic aldehyde or benzyl alcohol as the accelerator has also been studied. The results of our observations upon this point, together with all necessary data, are given in Table VIII.

It will be observed that the amount of nitrite formed increases with increase in the quantity of nitrate present. This increase, however, is by no means proportional to the amount of nitrate present. If it were, we should have 640 times as much nitrite formed in the experiments with 32 grams of nitrate as were produced in those in which 0.05 gram was employed, whereas in reality only about 10 times as much was formed. Relatively more nitrite is formed, therefore, when small amounts of nitrate are present. This has also been observed to be the case where the reduction is affected by the potato

Table VII.

Ten cc. potato extract; 2 cc. 35 per cent solution of potassium nitrate; 1 cc. water, or solution containing the indicated amount of accelerator.

Temperature, 40° C.

Time in hours.	Accelerator.	Amount of accelerator.	Nitrite in 2 cc. expressed in cc. of standard.	Total nitrite expressed in cc. of standard.	Amount of nitrite in milligrams.
1	Formaldehyde	1 cc. N/5 solution	0.120	0.780	0.17480
2	"	1 " N/5 "	0.170	1.105	0.24763
3	"	1 " N/5 "	0.210	1.365	0.30590
1	Acetaldehyde	1 " 4 per cent solution	0.240	1.560	0.34960
2	"	1 " 4 " "	0.375	2.437	0.54613
3	"	1 " 4 " "	0.400	2.600	0.58266
1	Benzaldehyde	0.1 cc.	0.650	4.225	0.94682
2	"	0.1 "	0.800	5.200	1.16532
3	"	0.1 "	0.950	6.175	1.38382
1	Ethyl alcohol	1 cc. 90 per cent	0.110	0.715	0.16023
2	"	1 " 90 " "	0.165	1.072	0.24024
3	"	1 " 90 " "	0.175	1.137	0.25480
1	Benzyl	0.1 cc.	0.675	4.387	0.98312
2	"	0.1 "	0.845	5.492	1.23075
3	"	0.1 "	0.975	6.337	1.42012

Table VIII.

Twenty cc. potato extract; amount of sodium nitrate used in each experiment given in column 3. In each experiment the volume was made up to 50 cc. with distilled water.

Time, one hour. Temperature, 40° C.

Accelerator.	Amount of accelerator.	Amount of nitrate in grams.	Nitrite in 2 cc. expressed in cc. of standard.	Total nitrite expressed in cc. of standard.	Amount of nitrite in milligrams.
Formaldehyde	1 cc. N/5 solution.	0.05	0.020	0.500	0.09115
"	1 " N/5 "	0.50	0.075	1.875	0.34183
"	1 " N/5 "	1.00	0.090	2.250	0.41019
"	1 " N/5 "	2.00	0.120	3.000	0.54693
"	1 " N/5 "	4.00	0.150	3.750	0.68366
"	1 " N/5 "	8.00	0.165	4.125	0.75202
"	1 " N/5 "	16.00	0.190	4.750	0.86597
"	1 " N/5 "	32.00	0.220	5.500	1.00270
Benzyl alcohol	0.5 cc.	0.05	0.025	0.625	0.11394
"	0.5 "	0.50	0.080	2.000	0.36462
"	0.5 "	1.00	0.140	3.500	0.63808
"	0.5 "	2.00	0.175	4.375	0.79760
"	0.5 "	4.00	0.190	4.750	0.86597
"	0.5 "	8.00	0.200	5.000	0.91155
"	0.5 "	16.00	0.210	5.250	0.95712
"	0.5 "	32.00	0.225	5.625	1.02549

extract alone. This in itself is doubtless an important consideration since in the plant only small amounts of nitrate are normally present in the cells, and hence the reduction must take place at great dilution. The effect of larger amounts of sodium nitrate on the reduction is similar to that of salts on other biochemical processes. It is well known that at great concentrations even neutral salts exert a toxic action on all changes of this character.

On the Effect of Increasing the Quantity of the Potato Extract on the Reduction in the Presence of an Accelerator.

That the amount of nitrite formed increases with the quantity of the potato extract, when the latter is acting in the presence of formic or benzoic aldehyde, may be seen from the experiments recorded in Table IX. In this series of experiments the increase in the quantity of nitrite formed seems to be greater than could be expected from the increase in the amount of potato extract. Whether this is really the case or due to some slight error, which up to this time we have been unable to detect, can only be determined by still further observations along this line.

On the Influence of the Mass of the Accelerator on the Reduction.

It seemed desirable to determine the influence of the mass of the accelerator on the rate of reduction. Formic aldehyde was the accelerator tried, partly for the reason of its activity, and partly because of the fact that it is readily soluble in water. The data relative to the experiments, together with the quantities of nitrite produced in each case, are given in Table X.

Corresponding controls showed none or only traces of nitrite. The solutions in the tubes to which formaldehyde of greater strength than $N/2$ had been added were diluted before they were tested for nitrite, as solutions containing such comparatively large quantities of formaldehyde were found to interfere with the nitrite test.

It will be observed that the first effect of increasing the quantity of formic aldehyde is to increase the amount of ni-

Table IX.

Amount of potato extract varied as indicated in column 3 of table; 2 cc. of 35 per cent solution of potassium nitrate; the whole made up to a total volume of 13 cc. with distilled water.

Time, one hour. Temperature, 40° C.

Accelerator.	Amount of accelerator.	Amount of potato extract in cc.	Nitrite in 2 cc. expressed in cc. of standard.	Total nitrite expressed in cc. of standard.	Amount of nitrite in milligrams.
Formaldehyde	1 cc. N/5 solution	1	0.005	0.032	0.00717
"	1 " N/5 "	2	0.010	0.065	0.01456
"	1 " N/5 "	3	0.025	0.162	0.03630
"	1 " N/5 "	4	0.035	0.227	0.05087
"	1 " N/5 "	5	0.045	0.292	0.06544
"	1 " N/5 "	6	0.060	0.390	0.08734
"	1 " N/5 "	7	0.075	0.487	0.10913
"	1 " N/5 "	8	0.090	0.585	0.13109
"	1 " N/5 "	9	0.110	0.715	0.16023
"	1 " N/5 "	10	0.120	0.780	0.17480
Benzaldehyde	0.1 cc.	1	0.001	0.006	0.00134
"	0.1 "	2	0.005	0.032	0.00717
"	0.1 "	3	0.015	0.097	0.02174
"	0.1 "	4	0.035	0.227	0.05087
"	0.1 "	5	0.050	0.325	0.07283
"	0.1 "	6	0.120	0.780	0.17480
"	0.1 "	7	0.150	0.975	0.21850
"	0.1 "	8	0.200	1.300	0.29133
"	0.1 "	9	0.250	1.625	0.36416
"	0.1 "	10	0.300	1.950	0.43700

trite produced. This reaches a maximum with N/5 formic aldehyde, however, after which any increase in the amount of the aldehyde causes a diminution in the quantity of nitrite formed. It would seem, therefore, from these results that at greater concentration formic aldehyde is poisonous to the reducing substance or substances in the potato, which effect these changes.

Table X.

Ten cc. potato extract; 2 cc. of 35 per cent solution of potassium nitrate; 1 cc. of solution containing the indicated amount of formic aldehyde.

Time, one hour.　　　　　　　　Temperature, 40° C.

Accelerator.	Amount of formic aldehyde.		Nitrite in 2 cc. ex-pressed in cc. of standard.	Total nitrite ex-pressed in cc. of standard.	Amount of nitrite in milligrams.
Formaldehyde	1 cc. N/50 solution		0.030	0.195	0.04370
"	1 "	N/10 "	0.230	1.495	0.33500
"	1 "	N/5 "	0.250	1.625	0.36416
"	1 "	N/2 "	0.160	1.040	0.23306
"	normal "		0.080	0.520	0.11653
"	1 cc. N/2 "		0.050	0.325	0.07283
"	1 "	N/5 "	0.020	0.130	0.02913
"	1 "	N/10 "	0.010	0.065	0.01457

On the Effect of Acids on the Reduction of Nitrates by Potato Extract in the Presence of an Accelerator.

The reduction of nitrates by the extract of the potato seems to take place best in a slightly acid medium. This is shown by the fact that even by simply neutralizing the very small amount of acid normally present in an active potato extract with alkali or lime-water its power to reduce a nitrate to nitrite is completely inhibited. It therefore occurred to us that it would be interesting to try the effect of acids on the progress of the reduction in the presence of an accelerator. This was tried, therefore, using a 4 per cent solution of formic aldehyde as an accelerator and N/10 solutions of the following

acids : hydrochloric, sulphuric, benzenesulphonic, *p*-nitro-toluenesulphonic, oxalic, formic, acetic, and butyric. The necessary data and results obtained are given in Table XI.

None of the controls contained any nitrite.

It will be observed that as a class acids exercise an inhibiting action on the progress of the reduction in the presence of an accelerator, the degree of inhibition depending upon the quantity of acid present and also on its strength, so that were we to arrange these acids with respect to their inhibitory effect on the change under consideration we would obtain the following : hydrochloric $=$ sulphuric $=$ benzenesulphonic $=$ *p*-nitrotoluenesulphonic $>$ oxalic $>$ formic $>$ acetic $>$ butyric. It has been found further that while large amounts of the weaker acids inhibit the reduction, in smaller quantities they considerably accelerate it, and even the stronger acids, such as hydrochloric, etc., seem to accelerate the reduction, if present in very small amounts. We observe therefore that, so far as the action of acids on the change here under investigation is concerned, the effect produced is similar to that which they exercise on zymotic processes in general.

The Behavior of Other Plant Extracts towards Nitrates.

A priori, there is no reason for supposing that the power to reduce nitrates is confined exclusively to the potato tuber. With the view of learning something further as to the occurrence and distribution of such reducing substances in the vegetable kingdom, aqueous extracts of the plants enumerated in Table XII. were prepared and tried.

It will be observed, therefore, that of the plants thus far examined, the egg plant and the potato, tuber and sprouts, are the only ones from which we have been able to prepare extracts capable of reducing nitrates to nitrites. In this connection it should be observed that since this investigation was first undertaken, Pozzi-Escot[1] found that aqueous extracts of the stems of the burdock had the power to reduce nitrates to nitrites and ammonia. He concludes that enzymes which reduce nitrates are very abundant in actively growing plants,

[1] This JOURNAL, **29**, 539.

Table XI.

Ten cc. potato extract; 2 cc. 35 per cent potassium nitrate; 1 cc. 4 per cent formaldehyde; 1 cc. water, or solution containing the indicated amount of acid.

Time, one hour.   Temperature, 40° C.

Name of acid.	Amount of acid.	Nitrite in 2 cc. expressed in cc. of standard.	Total nitrite expressed in cc. of standard.	Amount of nitrite in milligrams.
None	None	0.100	0.700	0.15687
Butyric	1 cc.	0.250	1.750	0.39217
Acetic	1 "	0.220	1.540	0.34511
Oxalic	1 "	0.185	1.295	0.29020
Formic	1 "	0.180	1.250	0.28236
Sulphuric	1 "	0.150	1.050	0.23530
Hydrochloric	1 "	0.140	0.980	0.21961
Benzenesulphonic	1 "	0.120	0.840	0.18824
p-Nitrotoluenesulphonic	1 "	0.110	0.770	0.17255
Butyric	2 "	0.170	1.190	0.26667
Acetic	2 "	0.140	0.980	0.21961
Oxalic	2 "	0.040	0.280	0.06274
Formic	2 "	0.050	0.350	0.07283
Sulphuric	2 "	0.000	0.000	0.00000
Hydrochloric	2 "	0.000	0.000	0.00000
Benzenesulphonic	2 "	0.000	0.000	0.00000
p-Nitrotoluenesulphonic	2 "	0.000	0.000	0.00000
Butyric	5 "	0.150	1.050	0.23530
Acetic	5 "	0.120	0.840	0.18824
Oxalic	5 "	0.000	0.000	0.00000
Formic	5 "	0.000	0.000	0.00000
Sulphuric	5 "	0.000	0.000	0.00000
Hydrochloric	5 "	0.000	0.000	0.00000
Benzenesulphonic	5 "	0.000	0.000	0.00000
p-Nitrotoluenesulphonic	5 "	0.000	0.000	0.00000

Table XII.

Ten cc. of the extract; 2 cc. of a 50 per cent solution of sodium nitrate ; 0.5 cc. of toluene as antiseptic.

Time, one hour.   Temperature, 40° C.

Name of plant.	Part of plant tested.	Amount of nitrite in millig'ms.
Potato[1] (*Solanum tuberosum*)	Tuber	0.10072
Egg plant (*Solanum melongena*)	Fruit	0.08195
Potato (*Solanum tuberosum*)	Sprouts, etiolated	0.02370
Artichoke (*Helianthus tuberosus*)	Tuber	None
Broom rape (*Orobanche ramosa*)	Entire plant	"
Radish (*Raphanus sativus*)	Root	"
Onion (*Allium Cepa*)	Bulb	"
Soy bean (*Glycine hispida*)	Leaves	"
Sweet potato (*Ipomoea batatas*)	Tuber	"
Apple (*Pyrus malus*)	Fruit	"
Banana (*Musa sapientum*)	"	"
Dahlia (*Dahlia variabilis*)	Tuber	"
Corn (*Zea mays*)	Unripe grain	"
Cinnamon vine (*Dioscorea divaricata*)	Axillary tuber	"
Coprinus atramentarius	Entire fungus	"
Wheat (*Triticum vulgare*)	Seedling	"
Buckwheat (*Fagopyrum esculentum*	"	"
Pea (*Pisum sativum*)	"	"
Barley (*Hordeum vulgare*)	"	"
Oats (*Avena sativa*)	"	"
Rye (*Secale cereale*)	"	"

especially at the end of a warm day. We have not yet had the opportunity to confirm this interesting and important observation. In connection with our failure to obtain extracts capable of reducing nitrates, it must be borne in mind that originally we experienced considerable difficulty in demonstrating this property satisfactorily even in the case of the potato, so that too much reliance cannot be placed in the negative results furnished by most of the plants examined. It may be that under slightly different conditions many, if not all of these, will still be found capable of reducing nitrates to nitrites. In this connection it has been found that the macera-

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[1] For sake of comparison the potato is included.

ted tissue of the potato sprout reduces nitrates better than the aqueous extract thereof, indicating that the reducing substances bringing about this change are only slowly dissolved out of the protoplasm. This fact should also be taken into account in the interpretation of our results with other plants, and still further work on this phase of the problem is necessary.

Summary and Discussion of Results.

To sum up briefly the results of this part of the investigation, it has been found that the potato and certain other plants contain a reducing substance or substances capable of effecting the reduction of nitrates to nitrites. It has been found further that the reduction takes place most rapidly at 40° to 45° C., that it is augmented by an increase in the amount of nitrate present and also by an increase in the quantity of the reducing extract, that it is inhibited by certain poisons and acids and greatly accelerated by certain other substances, especially by aldehydes and alcohols, and that plant extracts capable of effecting this reduction completely lose this property when heated to boiling. It has also been found that the reduction in the presence of accelerators is subject to such conditions as modify or alter the reduction of the nitrate by the potato extract alone. In other words, it would seem that the effect of the accelerator is simply to increase the activity of the extract, without fundamentally changing the course of the reaction. Finally, as has already been pointed out above, a remarkable parallelism exists between the change under consideration and those brought about by the soluble ferments. In this connection the question suggests itself, how far is this a real analogy ? While we are not yet in a position to answer this question satisfactorily, it should be observed that there has been a sort of loose tendency on the part of certain observers to put into the class of soluble ferments or enzymes all substances of animal or vegetable origin, which are destroyed in their aqueous solution by boiling, and which are more or less sensitive to the action of poisons. In consequence of this, an important property of the soluble ferment, namely, its

power to bring about chemical changes, in which the quantities of material changed are relatively very great and altogether disproportionate to the substance effecting the reaction, has apparently been lost sight of. Thus, for example, in biochemical oxidations and reductions there are many observations recorded which would indicate that the so-called oxidases and reductases are not enzymes in the strict sense of this definition. In fact, nearly all that is known concerning them goes to show that they enter only once into reaction, with the result that they themselves become so materially modified that they cannot act over again. Doubtless the fact that they are being continuously elaborated by the animal or plant has had a good deal to do with confusing them with the true enzymes. On the other hand, if with Berthelot[1] we look upon such an oxidizable substance as phosphorus as the prototype of these substances, we more nearly describe what they really can do, since phosphorus, whether acting as a reducing agent or a carrier of oxygen, is, likewise, limited in the oxidation and reduction which it can effect, the ultimate product of such reactions being phosphoric acid, a substance entirely incapable of inducing such changes. In this connection it should also be observed that while the number of oxygen carriers acting as true catalyzers in the sense that they are regenerated at the end of the chemical cycle, like platinum black and nitric oxide, is very limited, the number of other oxygen carriers is very large. In fact, if we admit the correctness of Engler's views of autoxidation, it follows that there are as many oxygen carriers as there are autoxidizable substances. Therefore, provisionally at least, we are inclined to put the reducing principles of the potato in the class of oxidizable substances, and to regard them as capable of reducing limited quantities of nitrate. At the same time we desire to call the attention of chemists to the necessity of finding some term other than fermentation whereby to distinguish such biochemical processes as the one here under consideration.

The Action of Accelerators on the Reduction—Traube's Views.

From a purely chemical standpoint the accelerating action

[1] Berthelot: Chimie Vegetale et Agricole, **3**, 183.

of certain substances, such as aldehydes and alcohols, on the reduction of nitrates by the potato extract is perhaps the most interesting feature of our results.

In this connection it is interesting to note that Traube in his Theorie der Fermentwirkungen called attention to certain similar changes. According to this observer the ferments possess the power to give up the oxygen removed from a second substance to a third, and just as the oxydases and ferments of putrefaction carry free oxygen to other substances, so the reducing ferments carry to other oxidizable substances the oxygen taken up as the result of reduction. In this connection he cites the fact that yeast reduces indigosulphuric acid better in the presence of sugar than without it. Here again this theory should be extended so as to include unstable substances resulting from vital activity, but not true ferments. It is conceivable, for example, that the reducing substances in the potato remove oxygen from the nitrate and in turn oxidize the aldehyde or other accelerator. In so doing, the original reducing substance might of course be regenerated as such, in which event the substance in question could once more enter into reaction and thereby ultimately reduce very large amounts of nitrate. It seems more probable, however, that a reducing substance sufficiently powerful to remove oxygen from potassium nitrate would retain a part at least of the oxygen thus removed, at the same time that it gave up a portion of it to the accelerator. The result would be that the reducing substance would be gradually oxidized, and hence unable to reduce disproportionately large amounts of nitrate.

As to the mechanism of the action of the accelerator but little is known at present. It may be that the acceleration is due to the fact that the affinity of two reducing substances for the oxygen of the nitrate, *viz.*, that of the reducing substance in the plant extract and that of the aldehyde or alcohol, is greater than the affinity of either alone. This would account for the increased production of nitrite resulting from the addition of the accelerator. Or it may be, as Traube believes, that the reducing substance of the plant alternately takes oxygen from the nitrate and gives it up to the accelerator. In

this event also the effect of such third substances would be to accelerate the change.

A third explanation suggests itself. The reduction of the nitrate by the reducing substance in the potato might also be brought about by the decomposition of water, the nascent hydrogen thus produced reducing the nitrate. The presence of a second reducing substance might then accelerate the reaction by virtue of its affinity for oxygen. This view derives considerable support from the fact that under anaerobic conditions certain of the unorganized ferments, such as the butyric acid ferment and other putrefying bacteria, can cause the evolution of hydrogen from fermenting liquids. It also derives support from the early work of Pollacci[1] on the evolution of hydrogen sulphide from grapes and other plants that have been sprinkled with sulphur, and also from the later work of de Rey-Pailhade[2] and Pozzi-Escot[3] on the formation of hydrogen sulphide by the action of philothion and the reductases on sulphur. According to the first of these observers, the production of hydrogen sulphide is due to the action of nascent hydrogen resulting from the decomposition of water. Traube also inclined to this view of the mode of action of the reducing ferments. It also derives support from the following considerations. In the second part of this paper it will be shown that a platinum zinc alloy has the power of reducing a nitrate to nitrite, and that this power is also greatly increased by certain accelerators, notably formaldehyde. Now it has been shown by Gladstone and Tribe[4] that the action of metallic couples in reducing nitrates is due primarily to the electrolytic decomposition of water by the metallic couple, the nascent hydrogen produced by the electrolysis reducing the nitrate, the oxygen combining with the metal. The explanation of de Rey-Pailhade[5] regarding the formation and action of the reducing substance which he has called philothion also involves the decomposition of water. Accord-

[1] Gazz. chim. ital., **5**, 451-460.

[2] Compt. rend., **106**, 1683-1684; **107**, 43-44, et seq.

[3] This JOURNAL, **29**, 517-563.

[4] J. Chem. Soc. (London), **33**, 150.

[5] Given by Pozzi-Escot in an article on the " Reducing Enzymes," This JOURNAL, **29**, 522.

ing to this author philothion is probably to be represented by the general formula RH_2, when this hydrogenizes sulphur or reacts with oxygen we have :

$$RH_2 + S = R + H_2S,$$
and $$RH_2 + O = R + H_2O.$$

The substance represented by R, however, may according to this observer, regenerate philothion by the combined action of it and an oxidizable substance R' on water. Thus :

$$R + H_2O + R' = RH_2 + R'O.$$
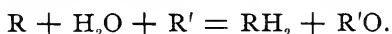
According to Pozzi-Escot[1] the reductases probably have an aldehyde nature in which case they probably effect the addition of hydrogen to such substances as sulphur by the decomposition of water. We observe therefore that all of these explanations have this in common, *viz.*, the idea that the hydrogen and oxygen necessary for these transformations are furnished by the decomposition of water.

A further interest attaches to our results on the action of aldehydes as accelerators in the reduction of nitrate by the potato extract. According to Gautier[2] the reduction of nitrates in the leaves of plants is accomplished by means of aldehydes. While our own results are not altogether in harmony with this view, it is interesting to note that the aldehydes do accelerate the reduction very greatly, and it is conceivable that in the plant normally the reduction of nitrate is effected not by any one reducing substance but by such a substance acting in the presence of an aldehyde, normally occurring in the cell. In this connection it should be observed that Curtius and Reinke[3] have obtained from the leaves of certain green plants a di- or tetrahydro aromatic aldehyde-alcohol to which they have assigned the formula

$$C_6H_6 \begin{cases} CHO \\ CH_2OH \end{cases} \quad \text{or} \quad C_6H_8 \begin{cases} CHO \\ CH_2OH \end{cases}.$$
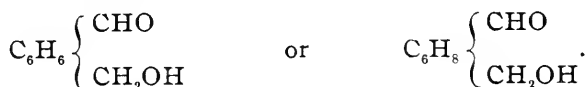
In the light of our results there can be but little question that

[1] Given by Pozzi-Escot in an article on the " Reducing Enzymes," This Journal, **29**, 561.

[2] Lecons de Chimie Biologique, Ed. **2**, p. 36.

[3] Ber. d. bot. Ges., **15**, 201.

such a compound would at least assist materially in the reduction of nitrates by the growing plant.

On the Reduction of Nitrates by Metals in the Presence of Accelerators.

Several years ago Loew[1] called attention to the fact that when platinum black, glucose, and potassium nitrate are brought together under certain conditions, ammonia is formed. It will be observed that this case presents a certain analogy to the reduction of a nitrate by the potato extract in the presence of an accelerator, the extract taking the place of the platinum black in Loew's experiment. The analogy becomes all the more striking when it is borne in mind that in both instances aldehydes function as accelerators. It therefore occurred to us to test the conduct of platinum black towards a nitrate, both in the presence and absence of an accelerator.

The platinum black employed in our first series of experiments was prepared by precipitating the metal from its chloride by means of zinc dust. The precipitate was washed by decantation, first with hydrochloric acid and finally with distilled water. It was then transferred to a filter and washed with distilled water until free from chloride. Finally it was thoroughly dried at ordinary temperature.

Series 1.—Three tubes were prepared as follows : No. 1 contained 0.1 gram platinum, 10 cc. water, 1 cc. of a 4 per cent solution of formaldehyde, and 2 cc. of a 50 per cent solution of sodium nitrate. No. 2 differed from No. 1 only in that it contained 1 cc. water in place of the 1 cc. of formaldehyde in the latter. No. 3 differed from No. 1 only in that it contained no platinum.

The tubes were tightly corked and shaken, and then allowed to remain at 40° C. for seventeen hours. At the end of this time the contents of each tube was tested for nitrite, and the amount of nitrite determined in the usual manner. The following results were obtained :

[1] Ber. d. chem. Ges., **23**, 675 (1890).

No. of experiment.	Total nitrite in milligrams.
I	2.37003
2	0.05925
3	0.00000

Series 2.—This differed from the above only in that the time allowed for the experiments was a little longer, namely, twenty-four hours.   The following results were obtained :

No. of experiment.	Total nitrite in milligrams.
I	3.37729
2	0.07110
3	0.00000

Series 3.—This was exactly similar to the above, except that the time was increased to forty-eight hours.   The following are the results obtained :

No. of experiment.	Total nitrite in milligrams.
I	4.26605
2	0.07703
3	0.00000

Series 4.—This differed from the former series in containing 1 cc. of 90 per cent alcohol as the accelerator in place of the 1 cc. of formaldehyde.   After standing for five hours the following results were obtained :

No. of experiment.	Total nitrite in milligrams.
I	0.56288
2	0.01185
3	0.00000

Series 5.—In this series 1 cc. of $N/10$ formic acid was used as the accelerator in place of the formaldehyde or alcohol in the former experiments.   A 35 per cent solution of potassium nitrate was also substituted for the 50 per cent solution of sodium nitrate used in the previous experiments.   After standing for two hours at 40° C. the following results were obtained :

No. of experiment.	Total nitrite in milligrams.
I	0.17775
2	0.00091
3	0.00000

Other substances which were found to work quite well as

accelerators in the case of the potato, such as benzaldehyde, benzyl alcohol, and vanillin, were also tried with platinum in place of the potato extract, but the results obtained were very indefinite, certainly not so striking as in the cases just given. While the cause of this apparent difference in the effect of these accelerators towards the potato extract and platinum has not yet been investigated, it is not unlikely that the reason of the inactivity of these substances is due to their insolubility, and thus unlike the system obtained with the potato extract, these furnish systems, with two insoluble substances which therefore have little chance of coming in contact with one another.

It is evident from these results, therefore, that sodium and potassium nitrates are reduced to nitrite by platinum black, and that the amount of nitrite so produced is greatly increased (from 10 to 60 times) by the presence of certain third substances, such as ethyl alcohol, formaldehyde, and formic acid.

On the Effect of Heat on the Reducing Power of Platinum.

In this connection it occurred to us to determine the effect of heat on the activity of platinum black as a reducing agent. In order to test this point a specimen of platinum, prepared as indicated above, was divided into three portions. One portion was kept at ordinary temperature, a second was heated to about 300° C. for about twenty or thirty minutes, and a third was heated to redness for the same length of time. With these three specimens the following experiments were tried :

Series 6.—No. 1. 0.1 gram platinum, that was not heated, was brought together in a test-tube with 11 cc. of water and 2 cc. of 35 per cent solution of potassium nitrate. No. 2. Same as (1), except that it contained 1 cc. of a 4 per cent solution of formaldehyde in place of 1 cc. of water as in (1). No. 3. Same as (1), except that 0.1 gram platinum that had been heated to about 300° C. was used in place of platinum at ordinary temperature. No. 4. Same as (2), except that 0.1 gram of platinum (heated to about 300° C.) was employed. No. 5. Same as (1) and (3), except that 0.1 gram of platinum that had been heated to redness for half an hour was

employed. No. 6. Same as (2) and (4), except that 0.1 gram of the platinum (heated to redness) was used.

The tubes containing these several substances were allowed to stand at 40° C. for four hours, at the end of which time the quantity of nitrite in each was determined. The following results were obtained :

No. of experiment.	Total nitrite in milligrams.
1	0.01457
2	0.14567
3	0.00000
4	16.02315
5	0.00000
6	2.03931

These results are of interest, first as showing that formaldehyde greatly accelerates the reduction of nitrate by platinum, just as it was found to in the case of the potato extract. In fact, with the platinum that had been heated to about 300° C., and to red heat, its presence seemed to be essential for the reduction, since no nitrite was formed when it was not at hand. The most interesting fact brought to light by these experiments, however, is that heat increases the activity of platinum black when acting in the presence of an accelerator, and that as compared with the activity of the metal that had been kept at ordinary temperature, and that which had been heated to redness, that which had been heated to about 300° C. was by far the most active.

Another series of experiments was tried with some of the same platinum black as that employed in Series 6. In this series some of the metal that had been previously heated to 100° C. and 300° C. respectively for thirty minutes was compared with some that had been kept at ordinary temperature. Six tubes were prepared. Nos. 1, 2, 3, and 4 were similar in every respect to Nos. 1, 2, 3, and 4 in the first series of experiments. Nos. 5 and 6 differed from the corresponding ones in Series 6, in that they each contained 0.1 gram of the platinum black that had been heated to 100° C. instead of that which had been heated to redness. These tubes were kept at 40° C. for three hours. At the end of this time the amount of nitrite was determined in each with the following results :

Number of experiment.	Total nitrite in milligrams.
1	0.01165
2	0.11653
3	0.00000
4	5.82660
5	0.00291
6	0.18936

It will be observed that while the activity of the platinum is slightly increased by heating it to 100° C. for half an hour, previous to the experiment, it by no means compares in activity with that which had been heated to 300° C.

In view of this remarkable increase in the reducing powers of the metal brought about by heating it to 300° C. it occurred to us to study the conduct of platinum black, prepared by other methods, towards a nitrate in the presence of an accelerator. Accordingly, platinum black was prepared by the following methods : By Loew's[1] method, by Zdrawkowitch's[2] method, by reducing platinum chloride with metallic magnesium and washing with hydrochloric acid, by reduction of the chloride with Kahlbaum's pure zinc and washing with acid, and by heating ammonium chlorplatinate to dull redness. The activity of these several varieties of the metal was tested in the manner already described in the experiments with platinum black obtained by the reduction of the chloride with zinc dust, Series 6. Strange to say, none of these specimens possessed the activity of the metal obtained by precipitating with zinc dust, and certain of them gave not even the slightest indication of the formation of nitrite. That obtained from ammonium chlorplatinate and by Loew's method gave only slight traces of nitrite. This is all the more remarkable when we consider that Loew's platinum black is said to be a very active variety of the metal, and one specimen of this was found by us to readily oxidize aldehydes in the presence of air. It therefore occurred to us that possibly the active platinum black, which was obtained by precipitating the metal with zinc dust, and also with stick zinc, contained other substances, in spite of the fact that in

[1] Ber. d. chem. Ges., **23**, 289 (1890).
[2] Ann. Chem. (Liebig), **181**, 192.

every case it had been washed with hydrochloric acid, and in some cases with both hydrochloric and nitric acids. The amount of platinum in these several specimens of the metal that had been prepared by means of zinc was therefore determined by the usual method of converting into ammonium chlorplatinate and weighing as platinum. The following are the results of several of these determinations :

		Per cent. of platinum.
1	Platinum black, obtained by precipitating with zinc dust and washing with dilute hydrochloric acid.	85.5
2	Same as (1) but stood under nitric acid over night.	89.45
3	Prepared by precipitating with pure stick zinc, and washing with dilute hydrochloric acid.	90.46
4	Obtained by precipitating with filings of Kahlbaum's pure stick zinc and washing with acid.	86.42

The metallic impurity in these several specimens was found to consist chiefly of zinc. It seems therefore that it is impossible to remove all of the zinc from platinum black that has been prepared by precipitating with this metal, by washing with dilute acids. This naturally suggests that the platinum black thus obtained is really an alloy of zinc and platinum, and that it owes its power to reduce a nitrate to the zinc which it contains. The effect of heat in increasing the activity is none the less interesting, however, and the question still remains to be considered, why is the activity of this material so greatly increased by heating to 300° C. ? While this question has not been satisfactorily answered as yet, it is interesting to note in this connection that Deville and Debray[1] have observed a curious change in the character of zinc alloys of certain of the platinum metals at 300° C., notably in the case of iridium. Some similar change then seems to occur in the platinum zinc alloy at this temperature. It has occurred to us that this change may consist in the lessening of the attraction of the zinc for the platinum in the alloy.

[1] Chem. Centrbl., 1882, 468; Compt. rend., **64**, 1557-60.

This would satisfactorily explain the increased activity of the material that has been heated to this temperature, since it is known that zinc itself rapidly reduces nitrates. On the other hand, we know from the work of Gladstone and Tribe[1] that certain couples of metals, as the copper-zinc couple, also reduce nitrates and effect other reactions with great rapidity. It may be therefore that the platinum-zinc alloy is really a couple of this description, and that the effect of the heat is to cause an alteration in the couple, whereby it becomes more active. It is known for example, that the activity of the so-called dry copper-zinc couple in certain reactions depends a great deal on the manner of heating the two metals in its preparation. However, all these matters require further investigation. We hope in the future to study the effect of such reducing-agents as formic aldehyde on the reduction of nitrate by metallic couples of various kinds. In fact, some evidence of the accelerating action of formic aldehyde in the reduction of nitrates by metallic couples has already been obtained.

On the Influence of Accelerators on the Reduction of Nitrate by Zinc-Silver Alloys.

The results reached in our study of the reduction of potassium nitrate by platinum black led us to test the conduct of precipitated silver towards a solution of the nitrate. In our first experiments finely divided silver was obtained by precipitating a dilute solution of silver nitrate with zinc dust, washing the precipitate first with dilute nitric acid and finally with distilled water. Under these conditions, the silver was obtained in the form of a grayish white powder. On analysis, it was found to consist entirely of metallic silver. It was found to be entirely inactive towards potassium nitrate even in the presence of an accelerator. This, then, is in keeping with our results with pure platinum black. On the other hand, when a strip of zinc is immersed in a dilute solution of silver nitrate the silver is obtained in the form of a loosely adhering black or very dark gray coating on the surface of the

[1] J. Chem. Soc. (London), **33**, 139, 151 (1878).

zinc. If this be removed from the surface of the zinc by constant stirring and washed with water, but not with acid, a dark grayish-black powder is obtained altogether different in appearance from the lighter silver-gray powder obtained by washing the precipitated silver with dilute nitric acid. On analysis, this dark powder was found to contain only 90.1 per cent. of metallic silver. This dark material therefore is in all probability a true alloy of zinc and silver analogous in composition to the platinum black obtained by precipitating platinum chloride with zinc dust. On adding acid to this dark-colored material it becomes grayish white in appearance and altogether similar to pure silver in finely divided condition. Ludtke[1] seems to regard this black silver sponge obtained by reducing silver nitrate with zinc as a distinct modification of metallic silver. He also has observed that acids transform it into the gray variety, and that this change is accompanied by an increase in the electrical conductivity of the material. His results can be better explained, however, on the supposition that the black sponge is an alloy of zinc and silver. Like the platinum-zinc alloy, this black silver sponge has been found to be an exceedingly active denitrifying material, especially when allowed to act upon the nitrate in the presence of certain other substances, such as formaldehyde.

That such is the case may be seen from the following experiments :

In order to determine the reducing power of this silver-zinc alloy three series of experiments were tried. In Series A three tubes were prepared. No. 1 contained 0.1 gram of the silver-zinc alloy, 10 cc. of water, 1 cc. 4 per cent formaldehyde, and 2 cc. of a 35 per cent solution of potassium nitrate. No. 2 was same as No. 1, except that it contained 1 cc. of water instead of 1 cc. of formaldehyde. No. 3 was the same as No. 1, except that it contained no metal. These tubes were kept at 40° C. for two hours.

Series B.—Nos. 1, 2, and 3 same as 1, 2, 3 in Series A, except that the tubes were heated to 40° C. for four hours.

[1] Ann. Phys. Chem. [2], **50**, 678, 695.

Series C.—Nos. 1, 2, and 3 same as corresponding experiments in Series A, except that the tubes were kept in the bath at 40° C. for fifteen hours.

At the end of these several intervals respectively, the several amounts of nitrite were determined colorimetrically, with the following results :

Series.	No. of experiment.	Total nitrite in milligrams.
A	1	7.86591
"	2	0.01456
"	3	0.00000
B	1	11.65320
"	2	0.02000
"	3	0.00000
C	1	21.84975
"	2	0.15000
"	3	0.00000

It is evident from these results that the amount of nitrite formed by the action of the silver-zinc alloy on potassium nitrate is greatly increased by the presence of small amounts of formaldehyde. Indeed, of all the substances thus far tried, formaldehyde has been found to be by far the most active. Whether, as was found in the case of the platinum-zinc alloy, heat increases the activity of the silver-zinc alloy still remains to be determined.

Up to the present only one phase of the process of denitrification, namely, the formation of nitrite by the several agencies herein mentioned, has engaged our attention. The formation of ammonia is doubtless also an important phase of this process. It is our intention to undertake an experimental study of this phase of the reduction as soon as time will permit, and also to investigate more thoroughly the effect of various reducing agents on the reduction of nitrates by various metallic couples.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, KENTUCKY,
October, 1903.

THE REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS.

I. REACTIONS OF UNSATURATED ALDEHYDES AND UNSATURATED KETONES.

By E. P. Kohler.

In a paper on "diphenylstyrylcarbinol"[1] I described the reaction between benzalacetophenone and phenylmagnesium bromide. The simplest substance obtained by this reaction was regarded as a tertiary alcohol represented by the formula $C_6H_5CH : CHC(OH)(C_6H_5)_2$. This view was based on the following facts:

1. The method of preparation would be expected to give a substance represented by the formula proposed. With saturated ketones Grignard's reaction gives tertiary alcohols, and, in all the cases that have been described, the products obtained from 1,2-unsaturated compounds are of the same kind as those obtained from the corresponding saturated compounds.[2]

2. The substance readily reacts with phosphorus pentachloride, the result being the elimination of an oxygen atom and a hydrogen atom, and the introduction of one chlorine atom.

3. The substance decolorizes a solution of bromine in carbon bisulphide in the cold. The product, which contains only 1 atom of bromine, was supposed to be formed by addition of bromine and subsequent loss of hydrobromic acid.

4. When oxidized with potassium permanganate the substance breaks down into benzophenone, benzoic acid, and carbon dioxide. This result was interpreted as follows:

$$\text{I. } C_6H_5CH : CHCOH(C_6H_5)_2 + 4O =$$
$$C_6H_5CO_2H + (C_6H_5)_2COHCO_2H ;$$

$$\text{II. } (C_6H_5)_2COHCO_2H + O = (C_6H_5)_2CO + H_2O + CO_2.$$
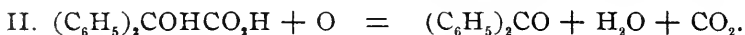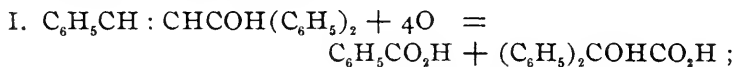
These results agreed with the proposed formula, but attention was drawn to the unexpected inertness of the hydroxyl

[1] This JOURNAL, **29**, 352.

[2] Ann. chim. phys., [7], **24**, 465-473; Ber. d. chem. Ges., **35**, 3188.

group in the carbinol and of the chlorine atom in the chloride. The substance was made with the expectation that the hydroxyl group would be as reactive as that of triphenylcarbinol and its behavior seemed inexplicable. Attention was also drawn to the fact that the substance forms no ether with alcohols and no esters with acid chlorides or acid anhydrides. This was attributed to the influence of the groups in combination with the tertiary carbon atom, since similar difficulties are met within the preparation of esters of triphenylcarbinol. Since the publication of the paper I have found that all these peculiarities are explained by the fact that the substance is not a tertiary alcohol at all, but an isomeric ketone represented by the formula

$$\begin{matrix} C_6H_5 \\ \diagdown \\ \diagup \\ C_6H_5 \end{matrix} CHCH_2COC_6H_5.$$
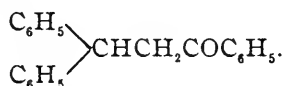
This formula is established by the following facts :

1. The substance forms a phenylhydrazone and an oxime.

2. By Beckmann's rearrangement the oxime passes into an acid anilide which, on hydrolysis, gives β,β-diphenylpropionic acid :

$$\text{I.} \quad \begin{matrix} C_6H_5 \\ \diagdown \\ \diagup \\ C_6H_5 \end{matrix} CHCH_2\underset{\underset{NOH}{\|}}{C}C_6H_5 \quad \longrightarrow \quad \begin{matrix} C_6H_5 \\ \diagdown \\ \diagup \\ C_6H_5 \end{matrix} CHCH_2CONHC_6H_5 ;$$

$$\text{II.} \quad \begin{matrix} C_6H_5 \\ \diagdown \\ \diagup \\ C_6H_5 \end{matrix} CHCH_2CONHC_6H_5 + H_2O =$$

$$(C_6H_5)_2CHCH_2CO_2H + C_6H_5NH_2.$$
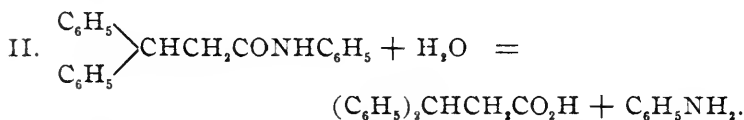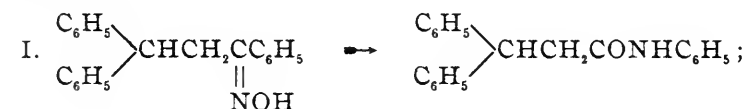
3. The substance can be made by condensing benzene with benzalacetophenone in the presence of concentrated sulphuric acid :

$$C_6H_5CH : CHCOC_6H_5 + C_6H_6 = (C_6H_5)_2CHCH_2COC_6H_5.$$
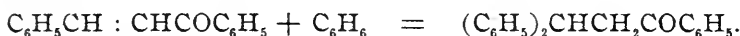
4. The substance reacts with phenylmagnesium bromide to form the same tertiary alcohol that is obtained by the action of phenylmagnesium bromide on the methyl ester of β,β-diphenylpropionic acid :

I. $(C_6H_5)_2CHCH_2CO.OCH_3 + 2C_6H_5MgBr =$
$$(C_6H_5)_2CHCH_2C(C_6H_5)_2OMgBr + MgOCH_3Br;$$

II. $(C_6H_5)_2CHCH_2COC_6H_5 + C_6H_5MgBr =$
$$(C_6H_5)_2CHCH_2C(C_6H_5)_2OMgBr.$$
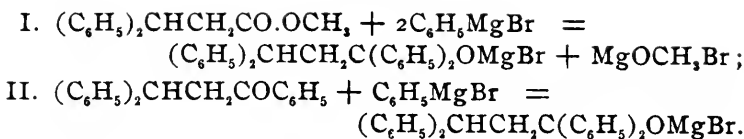
These results prove that the earlier formula is wrong and that the substance is β,β-diphenylpropiophenone. The facts used in support of the earlier formula are explained as follows:

1. The product of the reaction with phosphorus pentachloride is triphenylchlorpropylene,

$$(C_6H_5)_2CHCH = CClC_6H_5.$$
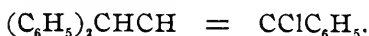
2. The action of bromine is direct substitution; the product, as will be shown below, is α-brom-β,β-diphenylpropiophenone, $(C_6H_5)_2CHCHBrCOC_6H_5$.

3. The oxidation with permanganate is represented by the equation:

$(C_6H_5)_2CHCH_2COC_6H_5 + 5O =$
$$(C_6H_5)_2CO + CO_2 + C_6H_5CO_2H + H_2O.$$
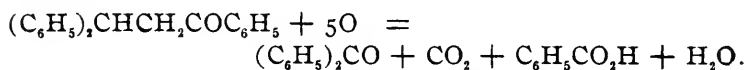
4. The dimolecular reduction-product is the pinacone

$$(C_6H_5)_2CHCH_2COHC_6H_5$$
$$\mid$$
$$(C_6H_5)_2CHCH_2COHC_6H_5$$
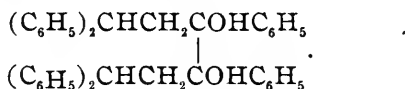
The formation of diphenylpropiophenone from benzalacetophenone illustrates a new kind of reaction of organic magnesium compounds. The only magnesium compounds that, when decomposed with water, would give this ketone, are represented by the formulas:

$$\begin{matrix} C_6H_5 \\ {\diagdown} \\ C_6H_5 \diagup \end{matrix} CH—CHCOC_6H_5 \qquad \begin{matrix} C_6H_5 \\ {\diagdown} \\ C_6H_5 \diagup \end{matrix} CH—CH=CC_6H_5$$
$$\qquad\qquad \mid \qquad\qquad\qquad\qquad\qquad\qquad \mid$$
$$\qquad\qquad MgBr \qquad\qquad\qquad\qquad\qquad\qquad OMgBr$$
$$\qquad\qquad\text{I.} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{II.}$$
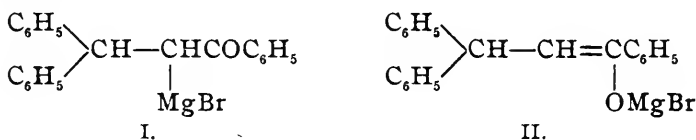
It follows that the phenylmagnesium bromide, in this case, does not combine with the carbonyl group as it does in the

case of saturated ketones ; but, either with the unsaturated carbon atoms of the chain—giving Formula I.—or at the extremities of the conjugated system, $C=C—C=C$, giving Formula II. The relation between these two formulas is exactly the same as that between the formulas used to represent the metallic derivatives of substances like acetoacetic ester. The properties of the magnesium compounds are essentially the same as those of the metallic derivatives referred to, so that this reaction makes it possible to get, indirectly, a number of reactive metallic derivatives of substances that do not have sufficiently mobile hydrogen atoms to form such derivatives by direct replacement.

The facts at present available are not sufficient to make it possible to decide, conclusively, between the two formulas, but I believe that Formula II. gives the simplest explanation of all the reactions that have been studied. When the magnesium compound is treated with water it yields diphenylpropiophenone, and when it is treated with bromine it yields α-brom-diphenylpropiophenone. These results are explained equally well by both formulas. The substance also reacts with acid chlorides. A substance with Formula I., which represents a compound of the type RMgBr, should give, with acid chlorides, a magnesium derivative of a tertiary alcohol. A substance with Formula II., on the other hand, should give an ester and a magnesium salt. The substance in question reacts with benzoyl chloride according to the equation :

$$\begin{array}{c} C_6H_5 \\ \diagdown \\ C_6H_5 \diagup \end{array} CH—CH = \underset{\underset{OMgBr}{|}}{C} C_6H_5 + C_6H_5COCl =$$

$$\qquad\qquad \begin{array}{c} C_6H_5 \\ \diagdown \\ C_6H_5 \diagup \end{array} CH—CH = \underset{\underset{OCOC_6H_5}{|}}{C} C_6H_5 + MgClBr.$$
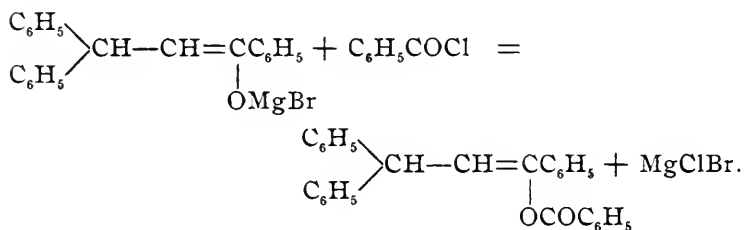
The reaction was carried out in a freezing-mixture and the amount of ester obtained was 98 per cent of the theoretical yield. The formation of this ester can, of course, be ex-

plained on the assumption that the structure of the magnesium compound is represented by Formula I. ; but as there is not the slightest evidence in favor of this formula, I prefer Formula II., which gives the result as one of direct replacement.

Moreover, a magnesium compound with the structure represented by Formula I. should react with saturated aldehydes and ketones, and with esters of saturated acids. I have tried five magnesium compounds of this type with seven different ketones and six esters, and have failed to get a reaction in a single case. These magnesium compounds readily combine, however, with unsaturated aldehydes, unsaturated ketones, and unsaturated esters, just as the metallic derivatives of acetoacetic ester combine with a variety of unsaturated compounds. The study of these addition-reactions has not been completed, hence the results will be reserved for a later paper.

A number of experiments have been made for the purpose of ascertaining to what extent α,β-unsaturated compounds combine with organic magnesium compounds in the manner just described in the case of benzalacetophenone. The work in this direction is not nearly complete, but the results already obtained indicate some of the factors that determine the course of the reaction between these substances.

The result is, in all probability, independent of the nature of the magnesium compound, since it has been found that methylmagnesium iodide, isopropylmagnesium bromide, phenylmagnesium bromide, benzylmagnesium chloride, and naphthylmagnesium bromide, give the same kind of reaction with a given unsaturated compound.

The result depends entirely upon the nature of the unsaturated compound. The following table gives the results that have been obtained with a selected list of typical unsaturated compounds. A comparison of these results with those obtained in other addition-reactions of the same substances will be given in a subsequent paper.

Summary of Reaction between α,β-Unsaturated Compounds and Organic Magnesium Compounds.

Compound	Reagent	Product	Reference
$CH_3CH=CHC{=}O$ ($-H$)	CH_3MgI	$CH_3CH=CHC(CH_3)(OH)(-H)$	Grignard: Ann. Chim. Phys., [7], **24**, 465.
$C_6H_5CH=CHC{=}O$ ($-H$)	CH_3MgI	$C_6H_5CH=CHC(CH_3)(OH)(-H)$	Sand and Singer: Ber. d. chem. Ges., **35**, 3185.
$C_6H_5CH=C{-}C{=}O$ ($-Br\ H$)	C_6H_5MgBr	$C_6H_5CH=C{-}C(C_6H_5)(OH)(-Br\ H)$	This paper.
$(CH_3)_2C=CHC{=}O$ ($-CH_3$)	CH_3MgI	$(CH_3)_2C=CHC(CH_3)(OH)(-CH_3)$	Grignard: *Ibid.*, **35**, 477.
$C_4H_9{-}CH=CHC{=}O$ ($-CH_3$)	CH_3MgI	$C_4H_9CH=CHC(CH_3)(OH)(-CH_3)$	Grignard: *Ibid.*, **35**, 478.
$C_6H_5CH=CHC{=}O$ ($-CH_3$)	C_6H_5MgBr	$C_6H_5CH=CHC(C_6H_5)(OH)(-CH_3)$	This paper.
$C_6H_5CH=CHC{=}O$ ($-C_6H_5$)	CH_3MgI	$(C_6H_5)(C_6H_5)CH{-}CH{-}CH_2C{=}O\ (-C_6H_5)$	" "

Summary of Reaction between α, β-Unsaturated Compounds and Organic Magnesium Compounds (Continued).

$C_6H_5CH=C-C=O$ $\quad\mid\quad\quad\mid$ $\quad CH_3\ C_6H_5$	C_6H_5MgBr	$\begin{array}{l}C_6H_5 \\ \\ C_6H_5\end{array}\Big\rangle CH-CH\ C=O$ $\qquad\qquad\mid\qquad\mid$ $\qquad\qquad CH_3\ C_6H_5$	"
$C_6H_5C=C\ C=O$ $\quad\mid\ \ \mid$ $\ CH_3\ H\ C_6H_5$	C_6H_5MgBr	$C_6H_5-C-CH_2C=O$ $\qquad\mid\qquad\quad\mid$ $\qquad CH_3\qquad C_6H_5$	"
$C_6H_5CH=CHCH=CHC=O$ $\qquad\qquad\qquad\qquad\mid$ $\qquad\qquad\qquad\quad C_6H_5$	C_6H_5MgBr	$C_6H_5=CH.CHCH_2C=O$ $\qquad\qquad\mid\qquad\quad\mid$ $\qquad\qquad C_6H_5\qquad C_6H_5$	Unpublished results. This laboratory.
$C_6H_5CH=CHC=O$ $\qquad\qquad\quad\mid$ $\qquad\qquad\ OCH_3$	C_6H_5MgBr	$\left.\begin{array}{l} C_6H_5 \\ \\ C_6H_5\end{array}\right\rangle CH.CH_2C=O$ $\qquad\qquad\qquad\mid$ $\qquad\qquad\qquad OCH_3$ and $\begin{array}{l}C_6H_5 \\ \\ C_6H_5\end{array}\Big\rangle CH.CH_2C=O$ $\qquad\qquad\qquad\mid$ $\qquad\qquad\qquad C_6H_5$	"
$C_6H_5CH=C-C=O$ $\qquad\qquad\mid\quad\mid$ $\qquad\ C_6H_5\ OCH_3$	C_6H_5MgBr	$\begin{array}{l}C_6H_5 \\ \\ C_6H_5\end{array}\Big\rangle CH.CH\ C=O$ $\qquad\qquad\qquad\mid\quad\mid$ $\qquad\qquad\ C_6H_5\ OCH_3$	"

Method of Procedure. When a solution of an unsaturated ketone is gradually added to an ethereal solution of an organic magnesium compound, an amorphous precipitate invariably separates at once. At first this precipitate redissolves rapidly, but as the reaction proceeds the solution takes place more and more slowly until, finally, the precipitate no longer disappears when the liquid is shaken vigorously. Up to this point only one substance is formed. If more ketone is added the result is a mixture from which it is difficult to separate pure substances. The precipitate usually redissolves until the solution contains approximately half a molecule of ketone for every molecule of the magnesium compound; but somewhat more ketone can be used at low than at high temperatures.

In all the experiments with ketones the reaction was carried out as follows : An ethereal solution of the ketone was added, drop by drop, to a similar solution of the magnesium compound that was kept below —10°, until a permanent precipitate formed in the liquid. The mixture was then removed from the freezing-mixture and allowed to remain at the temperature of the laboratory for several hours, after which it was carefully decomposed with ice and the magnesium salts dissolved in iced hydrochloric acid. The organic product was dissolved in ether, the ethereal solution dried over calcium chloride, and the ether evaporated in a rapid current of dry air. The solids that separated were purified by recrystallization from alcohol.

I. Reactions with Benzalacetophenone.

1. Benzalacetophenone and Phenylmagnesium Bromide : Diphenylpropiophenone, $(C_6H_5)_2CHCH_2COC_6H_5$.—The analysis and properties of this substance were published in a previous paper. I tried to prepare it from diphenylpropionic acid and benzene by the Friedel and Crafts reaction. Five grams of aluminium chloride were added to a solution of 20 grams of diphenylpropionyl chloride in 50 grams of benzene that was kept cool with running water. The substances reacted in the

cold and the reaction was complete in a very short time.   The
product, isolated in the usual way, was a solid melting at 78°.
Analysis and properties showed that the substance is keto-
phenyldihydroindene, formed according to the equation :

$$\begin{matrix} C_6H_5 \\ \\ C_6H_5 \end{matrix}\Big\rangle CHCH_2COCl \;=\; \underset{\underset{C_6H_4-CO}{\big|\quad\big|}}{C_6H_4CHCH_2} + HCl.$$
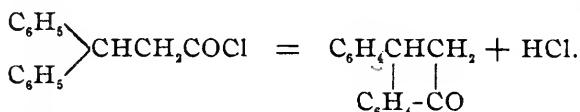
The yield was 13 grams.   While the ketone cannot be made
by the Friedel and Crafts reaction, it is easily obtained by di-
rect condensation of benzalacetophenone and benzene.   A
solution of 10 grams of benzalacetophenone in 100 grams of
benzene was treated with 10 grams of concentrated sulphuric
acid.   After shaking the mixture mechanically for six days,
the benzene layer was separated, washed with water, and dis-
tilled with steam.   The residue—six grams—was almost pure
diphenylpropiophenone.

The phenylhydrazone of diphenylpropiophenone was obtained
by boiling an alcoholic solution of the ketone with a slight
excess of phenylhydrazine for eight hours.   The product was
purified by recrystallization from alcohol.   It crystallizes in
pale yellow needles that melt at 137°.   The analyses give the
following results :

I. 0.1793 gram substance gave 0.5625 gram CO_2 and 0.1045
gram H_2O.

II. 0.4868 gram substance gave 32.2 cc. N at 20° and 756
mm.

	Calculated for $C_{27}H_{24}N_2$.	I.	II.
C	86.11	85.97	....
H	6.35	6.48	....
N	7.45	....	7.49

The oxime was made by boiling an alcoholic solution of 10
grams of the ketone, 10 grams of hydroxylamine hydrochlo-
ride, and 18 grams of potassium hydroxide for four hours.
The mixture was poured into cold water and the precipitated
oxime recrystallized from aqueous alcohol.   The oxime crys-
tallizes well in large, lustrous needles.   The melting-point is
at 131°.   An analysis gave the following results :

I. 0.1798 gram substance gave 0.5510 gram CO_2 and 0.1061 gram H_2O.

II. 0.6101 gram substance gave 26.3 cc. N at 21° and 756 mm.

	Calculated for $C_{21}H_{19}ON$.	Found.	
		I.	II.
C	83.72	83.56	....
H	6.31	6.55	....
N	4.65	....	4.93

Diphenylpropionanilide was obtained from the oxime of diphenylpropiophenone by Beckmann's rearrangement. For this purpose 5 grams of phosphorus pentachloride were added to an equal weight of the oxime dissolved in absolute ether. When the reaction was over, the ether was removed by distillation and the oily residue boiled with water until it had solidified completely. The anilide was purified by recrystalization from aqueous alcohol. It crystallizes in needles melting at 167°. It is readily soluble in alcohol and ether, sparingly soluble in ligroin.

0.1581 gram substance gave 0.4846 gram CO_2 and 0.0911 gram H_2O.

	Calculated for $C_{21}H_{19}ON$.	Found.
C	83.72	83.59
H	6.31	6.40

The anilide was hydrolyzed by heating it with hydrochloric acid in a sealed tube at 150°. The resulting acid was recrystallized from weak alcohol. It melted at 147°. It was compared with a specimen of β,β-diphenylpropionic acid prepared by condensing benzene with cinnamic acid. A mixture of the two melted sharply at 147°—the melting-point of pure diphenylpropionic acid.

Diphenylethyldiphenylcarbinol, $(C_6H_5)_2CHCH_2COH(C_6H_5)_2$.—When benzalacetophenone is treated with phenylmagnesium bromide the reaction always stops after the introduction of one phenyl group. To determine whether this is due to the properties of the resulting magnesium compound or to the combination of groups present in the substance, the ketone

obtained by decomposing the magnesium compound with
water was treated with phenylmagnesium bromide in the
usual way. The product has almost exactly the same melt-
ing-point as the ketone used in the reaction. A mixture of
the two, however, begins to melt 20° lower and the analysis
shows that it is a different substance.

0.1501 gram substance gave 0.4924 gram CO_2 and 0.0896
gram H_2O.

	Calculated for $C_{27}H_{24}O$.	Found.
C	89.01	89.4
H	6.59	6.63

The carbinol is readily soluble in alcohol and ether, mod-
erately soluble in ligroin. It crystallizes in needles that melt
at 95° to 96°. The same substance is obtained by treating
the methyl ester of diphenylpropionic acid with phenylmag-
nesium bromide. This result proves that it is the tertiary alco-
hol represented above. The alcohol cannot be made by treat-
ing the magnesium compound, that gives diphenylpropio-
phenone when decomposed with water, with an excess of
phenylmagnesium bromide. This result would be expected
if, as seems probable, the structure of the magnesium com-
pound is different from that of the ketone, namely,

$$(C_6H_5)_2CH.CH=C\begin{cases} OMgBr \\ C_6H_5 \end{cases}.$$
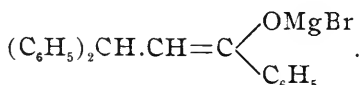
It may, however, be due to the influence of the α-substituent
in a compound of the structure

$$(C_6H_5)_2CH.CHCOC_6H_5,$$
$$| $$
$$MgBr$$
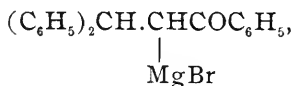
since results obtained with unsaturated acids show that some
α-substituents diminish the reactivity of the carbonyl group
towards organic magnesium compounds.

Bromdiphenylpropiophenone, $(C_6H_5)_2CHCHBrCOC_6H_5$. —
This substance was described in a previous paper. It is very
easily obtained when the magnesium compound formed in the

reaction between benzalacetophenone and phenylmagnesium bromide is treated with bromine. The ketone and the magnesium compound were brought together in the usual way. After the mixture had stood for four hours an ethereal solution of bromine was added, drop by drop, until the color of bromine no longer disappeared. This required 2 atoms of bromine for each atom of magnesium used in the preparation of the magnesium compound. When the mixture was poured into dilute hydrochloric acid, the product separated in colorless needles. After one crystallization from a mixture of chloroform and alcohol it melted sharply at 173°. The amount of pure substance obtained was 98 per cent of that calculated from the amount of ketone that had been used.

Benzoyltriphenylpropenol, $\begin{matrix} C_6H_5 \\ \diagdown \\ C_6H_5 \diagup \end{matrix} CHCH = C \underset{\underset{OCOC_6H_5}{|}}{C_6H_5}$. — The
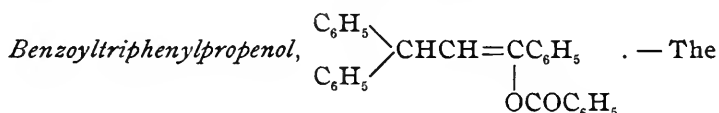
magnesium compound that is formed in the reaction between benzalacetophenone and phenylmagnesium bromide reacts with benzoyl chloride in the cold. An ethereal solution of the chloride was added to a mixture of the ketone and phenylmagnesium bromide, that had been prepared in the usual way and then cooled to —20° in a freezing-mixture. Each drop of the chloride produced a white precipitate until the mixture contained 1 molecule of benzoyl chloride for each atom of magnesium. The solid cake obtained in this way was immediately treated with iced hydrochloric acid, washed thoroughly with cold hydrochloric acid, alcohol, and ether, and dried in a current of air. The crude product melted at 218° to 220°. It was dissolved in boiling chloroform and precipitated with hot absolute alcohol. It was thus obtained in long transparent needles that melted at 220°. An analysis gave the following results :

0.1901 gram substance gave 0.6005 gram CO_2 and 0.0962 gram H_2O.

	Calculated for $C_{28}H_{22}O_2$.	Found.
C	86.15	86.14
H	5.64	5.67

The substance is moderately soluble in boiling chloroform and in boiling benzene, very slightly soluble in alcohol, ether, and acetone.

The two possible formulas for a substance of this composition and origin are the following :

$$\begin{matrix} C_6H_5 \\ \diagdown \\ \diagup \\ C_6H_5 \end{matrix} CHCHCOC_6H_5 \qquad \begin{matrix} C_6H_5 \\ \diagdown \\ \diagup \\ C_6H_5 \end{matrix} CH-CH=CC_6H_5$$

$$\begin{matrix} | \\ COC_6H_5 \end{matrix} \qquad\qquad\qquad \begin{matrix} | \\ O.COC_6H_5 \end{matrix}$$

I.   II.
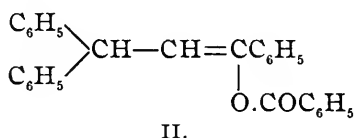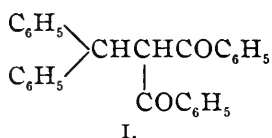
Formula I. represents an alkyldibenzoylmethane—a β-diketone—which should be soluble in alkalies and which should form metallic derivatives. Formula II. represents an ester of benzoic acid which should be insoluble in alkalies, should form no metallic derivatives, but should be easily hydrolyzed to benzoic acid and diphenylpropiophenone :

$$\begin{matrix} C_6H_5 \\ \diagdown \\ \diagup \\ C_6H_5 \end{matrix} CH-CH=CC_6H_5 + KOH =$$

$$\begin{matrix} | \\ OCOC_6H_5 \end{matrix}$$

$$C_6H_5CO_2K + \left[\begin{matrix} C_6H_5 \\ \diagdown \\ \diagup \\ C_6H_5 \end{matrix} CH-CH=CC_6H_5 \\ | \\ OH \right] \longrightarrow$$

$$\begin{matrix} C_6H_5 \\ \diagdown \\ \diagup \\ C_6H_5 \end{matrix} CH-CH_2COC_6H_5.$$
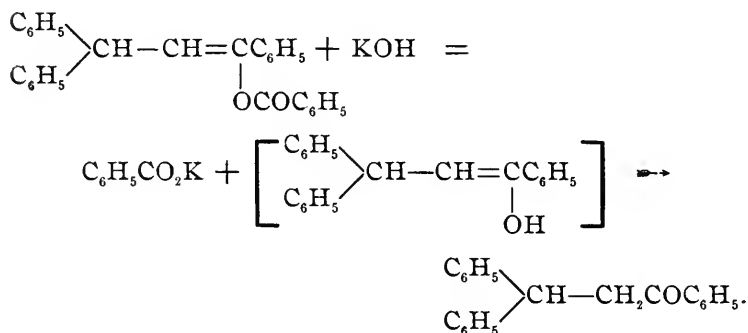
The substance under consideration is insoluble in alkalies, even in a cold solution of sodium alcoholate in alcohol ; its solution in ether gives no copper compound when treated with copper acetate and ammonia ; it gives no sodium derivative when its solution in ether or benzene is heated with metallic sodium. When it is warmed with a strong solution of potassium hydroxide to which a few drops of alcohol have been added, it first turns intensely yellow, then melts down to a colorless oil that solidifies on cooling. The solution contains potassium benzoate. The insoluble substance is pure

diphenylpropiophenone. The structure of the substance is, therefore, represented by Formula II.

2. *Benzalacetophenone and Methylmagnesium Iodide : Phenyl-butyrophenone,* $\begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\!\!>\!\!CHCH_2COC_6H_5$.—The reaction was carried out in the usual way. The product crystallizes from alcohol in large, colorless plates melting at 74°. It is very soluble in alcohol and in ether, moderately soluble in ligroin.

0.1890 gram substance gave 0.5720 gram CO_2 and 0.1209 gram H_2O.

	Calculated for $C_{16}H_{16}O$.	Found.
C	85.71	86.00
H	7.14	7.10

The same substance has recently been described by Harries,[1] who obtained it by reducing dypnone :

$$\begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\!\!>\!\!C\!\!=\!\!CHCOC_6H_5 + H_2 = \begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\!\!>\!\!C.CH_2COC_6H_5.$$
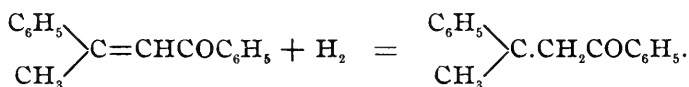
Harries gives a little lower melting-point (72°), but the melting-point of the hydrazone made from my product was found to be 79°, as given by Harries.

The *oxime* was obtained by boiling an alcoholic solution of the ketone with hydroxylamine hydrochloride and potassium hydroxide. It is very soluble in alcohol and ether. It crystallizes from aqueous alcohol in needles that melt at 93°.

0.1543 gram substance gave 0.4550 gram CO_2 and 0.0992 gram H_2O.

	Calculated for $C_{16}H_{17}ON$.	Found.
C	80.33	80.42
H	7.11	7.14

II. Reactions with Benzalpropiophenone.

1. *Preparation of Benzalpropiophenone.*—A mixture of equivalent quantities of benzaldehyde and propiophenone was saturated with gaseous hydrochloric acid and allowed to remain

[1] Ann. Chem. (Liebig), **330**, 223.

in ice-water for two days. The resulting greenish-yellow liquid was dissolved in ether, the ethereal solution washed with water, and extracted with a saturated solution of sodium bisulphite. After drying the solution with calcium chloride and removing the ether by distillation, there remained a pale-yellow oil that solidified almost completely when cooled in a freezing-mixture. The solid was recrystallized from low-boiling ligroin until it melted sharply at 83°. On analysis it was found to be benzylchlorpropiophenone,

$$C_6H_5CHClCHCOC_6H_5.$$
$$|$$
$$CH_3$$
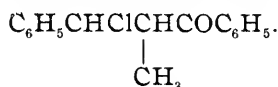
0.3384 gram substance gave 0.9285 gram CO_2 and 0.1807 gram H_2O.

	Calculated for $C_{16}H_{15}ClO$	Found.
C	74.20	74.17
H	5.85	6.13

The compound begins to lose hydrochloric acid a few degrees above the melting-point. It was, therefore, heated under diminished pressure as long as hydrochloric acid was given off, and finally distilled under a pressure of 28 mm. The entire product distilled between 190° to 192°. The distillate did not solidify in a freezing-mixture. The analysis shows that it was pure benzalpropiophenone.

0.1601 gram substance gave 0.5066 gram CO_2 and 0.0924 gram H_2O.

	Calculated for $C_{16}H_{14}O$.	Found.
C	86.49	86.31
H	6.30	6.41

The *phenylhydrazone*, made for the purpose of identification, crystallizes from alcohol in lemon-yellow needles that melt at 131°. The analyses gave the following results :

I. 0.1487 gram substance gave 0.4595 gram CO_2 and 0.0923 gram H_2O.

II. 0.2165 gram substance gave 0.6792 gram CO_2 and 0.1245 gram H_2O.

	Calculated for $C_{22}H_{20}N_2$.	I.	Found. II.
C	84.61	84.29	84.50
N	6.42	6.80	6.64

2. Reaction between Benzalpropiophenone and Phenylmagnesium Bromide: Diphenylisobutyrophenone, $\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!\!CH-$
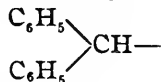
CHCOC$_6$H$_5$.—The substances react energetically even at low
|
CH$_3$

temperatures. The ketone separates in crystalline form when the magnesium compound is decomposed with iced hydrochloric acid. The yield of pure ketone is 96 per cent of the calculated amount. An analysis gave the following results:

0.2325 gram substance gave 0.7522 gram CO_2 and 0.1403 gram H_2O.

	Calculated for $C_{22}H_{20}O$.	Found.
C	88.00	88.23
H	6.67	6.70

The ketone is readily soluble in alcohol and ether, moderately soluble in ligroin. It crystallizes from alcohol in needles, from ligroin in large transparent plates. It melts at 105°. It is not oxidized by cold permanganate.

The *oxime* was made by boiling an alcoholic solution of the ketone with hydroxylamine hydrochloride and potassium hydroxide. The product was precipitated with water and recrystallized from weak alcohol. It is readily soluble in alcohol and ether. It crystallizes in needles that melt at 145°.

0.1510 gram substance gave 0.4629 gram CO_2 and 0.0910 gram H_2O.

	Calculated for $C_{22}H_{21}ON$.	Found.
C	83.81	83.60
H	6.66	6.70

III. Reaction with Dypnone.

1. Preparation.—At first dypnone was prepared by the method of Delacre, but the yield was small—about 27 per

cent of the calculated amount. In a second preparation the method was modified as follows: One hundred grams of acetophenone were dissolved in an equal weight of glacial acetic acid and the solution saturated with hydrochloric acid at the temperature of running water. After standing for twenty-four hours the mixture was heated under diminished pressure in a water-bath for two hours and then fractionally distilled under a pressure of 28 mm. The yield was 62 grams of pure ketone. No acetophenone was left over. The residue, after distillation, was mainly triphenylbenzene.

2. *Reaction with Phenylmagnesium Bromide: β,β-Diphenyl-*

$$C_6H_5\diagdown$$
butyrophenone, C_6H_5—C—$CH_2COC_6H_5$. —— Phenylmagnesium
$$CH_3\diagup$$

bromide reacts much more slowly with dypnone than with the ketones previously described. The product crystallizes in thick prisms or tables melting at 103°. It is readily soluble in alcohol, acetone, and ether; moderately soluble in ligroin. It is not oxidized by cold permanganate.

0.1065 gram substance gave 0.3440 gram CO_2 and 0.0631 gram H_2O.

	Calculated for $C_{22}H_{20}O$.	Found.
C	88.00	88.08
H	6.66	6.58

The *oxime* was made by boiling an alcoholic solution of the ketone with hydroxylamine hydrochloride and potassium hydroxide. It is moderately soluble in alcohol and in ether. It crystallizes in needles melting at 163°.

0.1385 gram substance gave 0.4251 gram CO_2 and 0.0840 gram H_2O.

	Calculated for $C_{22}H_{21}ON$.	Found.
C	83.81	83.70
H	6.66	6.73

IV. Reaction with Benzalacetone.

Grignard allowed methylmagnesium iodide to react with

benzalacetone and obtained a hydrocarbon, presumably formed by loss of water from an intermediate tertiary alcohol. When phenylmagnesium bromide reacts with benzalacetone the changes observed are exactly like those observed in the case of benzalacetophenone. A colored magnesium compound separates out and redissolves when the liquid is shaken. After the mixture has stood for some time a new magnesium compound separates as a colorless paste. No solid substances are obtained when this paste is decomposed with ice and hydrochloric acid. The product is an oil from which no solid substances could be obtained, either by prolonged exposure to low temperatures or by distillation with steam. When heated under diminished pressure the liquid remained clear until the temperature of the bath was 178°. At this point it suddenly became cloudy while water began to condense in the receiver. This indicated that the substance was not a ketone but an alcohol, and a test with permanganate showed that, unlike the ketones described above, it reduced a cold neutral solution of potassium permanganate. A new preparation of the substance was therefore made and oxidized as follows :

Twenty grams of the substance were suspended in a liter of water that was kept at 0° with cracked ice. To this liquid a cold saturated solution of potassium permanganate was added, in small portions, until the color remained after vigorous shaking. The oxides of manganese were filtered off and the filtrate acidified. The precipitate that formed was pure benzoic acid. The filtrate from the benzoic acid was evaporated to 250 cc. and cooled. The crystals that separated were again almost pure benzoic acid. The filtrate from this was distilled in a current of steam to remove the last traces of benzoic acid, and, finally, evaporated to a very small volume. The acid that separated on cooling was almost pure atrolactic acid. After one recrystallization from water it melted at 89° to 90° ; after driving off the water of crystallization on the water-bath it melted at 95°. When boiled with concentrated hydrochloric acid and distilled with steam atropic acid, melting at 104°, passed into the distillate.

These products of oxidation—benzoic acid and atrolactic

acid—show that the substance obtained from benzalacetone is

the tertiary alcohol, $C_6H_5CH : CHC\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_3}{-OH}}$, the oxidation

taking place according to the equation :

$$C_6H_5CH : CHC\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_3}{-OH}} + 4O \ =$$

$$C_6H_5CO_2H + CO_2H.C\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_3}{-OH}} .$$
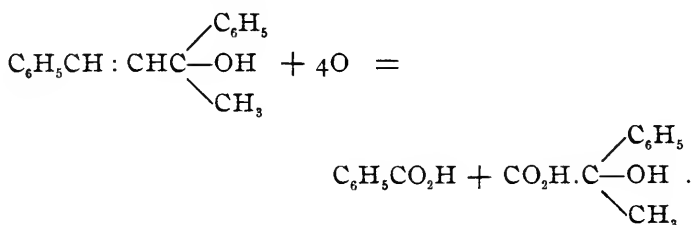
V. *Reaction with Cinnamic Aldehyde and α-Bromcinnamic Aldehyde.*

Sand and Singer treated cinnamic aldehyde with methyl-magnesium iodide and obtained a secondary alcohol. The main object of the following experiment was to ascertain whether the reaction goes exclusively in this direction. Cinnamic aldehyde was added to an ethereal solution of phenyl-magnesium bromide that was kept at —22°. The product, isolated in the usual way, was an oil that did not solidify in a freezing-mixture. One-half of the entire product was oxidized with potassium permanganate, the remainder boiled with hydroxylamine hydrochloride and potassium hydroxide. The oxidation was carried out in benzene solution. The substance was dissolved in twenty times its volume of pure benzene and this solution shaken with an iced 1 per cent solution of potassium permanganate that contained 1 atom of available oxygen for every molecule of the substance. After complete reduction of the permanganate, the benzene solution was separated and the benzene removed by distillation from the water-bath. The residue was a yellow oil that partially solidified on standing. The yellow solid was filtered off and recrystallized from ligroin. After one crystallization it melted at 50°, the melting-point of benzalacetophenone. The oil was distilled with steam. Only brombenzene passed into the dis-

tillate. The residue solidified completely on cooling. It was almost pure benzalacetophenone. The aqueous solution left after separating the benzene contained only benzoic acid. Judging by the behavior on oxidation, the product contained only the secondary alcohol, $C_6H_5CH : CHCHOHC_6H_5$, which was oxidized as follows :

$$C_6H_6CH : CHCHOHC_6H_5 + O =$$
$$C_6H_5CH : CHCOC_6H_5 + H_2O.$$
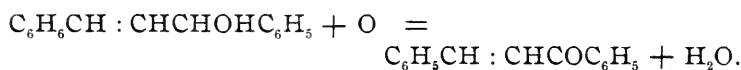
No oxime was obtained in the experiment with hydroxylamine.

The carbonyl group of α-bromcinnamic aldehyde is much less reactive than that of cinnamic aldehyde : it does not condense with acetophenone in the presence of alkalies, nor with malonic acid in the presence of acetic acid or acetic anhydride. It seemed possible, therefore, that the aldehyde might take up organic magnesium compounds in the 1,4-positions. The experiment was carried out exactly like that with cinnamic aldehyde and the result was the same. No trace of a saturated aldehyde could be detected in the product.

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THE CONSTITUTION OF PURPURIC ACID AND OF MUREXIDE.[1]

BY MAX SLIMMER AND JULIUS STIEGLITZ.

Of the many remarkable products that may be obtained from uric acid, perhaps none more excited the interest of older chemists, or has proven more valuable as the basis of a sensitive qualitative test in the physiological and chemical study of this group, than murexide. First observed by Scheele, Prout[2] later isolated it in crystalline form by the oxidation of uric acid with nitric acid and subsequent treatment with ammonia. To the crystalline substance so obtained he gave the name of purpurate of ammonia, and by

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[1] All the experimental work described in this paper was carried out by Dr. Slimmer.   J. STIEGLITZ.

[2] Phil. Trans., 1818, p. 420.

double decomposition he formed a number of other salts. By treatment with acids he obtained from the highly colored salts a colorless substance which he considered to be the free purpuric acid. Liebig and Wöhler[1] soon showed that this body was not the only product of the action of acids on the purpurates. Their investigations on the action of ammonia on alloxantin and on the oxidation of uramil to murexide include almost all that we know to this day of the chemistry of these substances. It was, however, left for Beilstein[2] to show that the reaction between alloxan and uramil is not as Liebig and Wöhler assumed, an oxidation, but a true condensation, occurring in alkaline solutions. Free purpuric acid is not stable, but on liberation by acids in aqueous solutions is at once decomposed into uramil and alloxan. As in best accord with these facts, Beilstein proposed the following constitution,

$$
\begin{array}{cccccccc}
NH & \!\!\!-\!\!\!- & CO & NH & & CO & \!\!\!-\!\!\!- & NH \\
| & & | & \diagdown & \diagup & | & & | \\
CO & & C & \!\!\!-\!\!\!-\!\!\!- & C & & & CO \\
| & & | & & | & & & | \\
NH & \!\!\!-\!\!\!- & CO & & CO & \!\!\!-\!\!\!- & NH \\
\end{array}
$$

I.
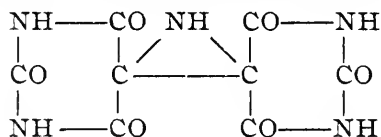
for purpuric acid, which is now commonly accepted.[3]

In his lectures one of us has already for many years expressed great doubt as to the correctness of this constitution for purpuric acid and has suggested the following linking of the carbon and nitrogen atoms as more clearly expressing its reactions :[4]

$$
\begin{array}{ccccccc}
1\ NH & \!\!-\!\!\!- & CO\ 6 & 6'\ CO & \!\!-\!\!\!- & NH\ 1' \\
| & & | & | & & | \\
2\ CO & 5\ CH & \!\!-\!\!N & = & C\ 5' & CO\ 2' \\
| & & | & | & & | \\
3\ NH & \!\!-\!\!\!- & CO\ 4 & 4'\ CO & \!\!-\!\!\!- & NH\ 3' \\
\end{array}
$$
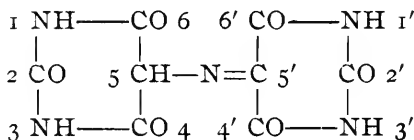
II.

Its formation from uramil and alloxan in alkaline solutions

[1] Ann. Chem. (Liebig), **26**, 241 (1838).

[2] *Ibid.*, **107**, 241 (1858).

[3] Compare Beilstein, Vol. I., 1340. Also Meyer and Jacobson, Vol. I., 1082. See, however, Bernthsen's "Lehrbuch der organischen Chemie," p. 291.

[4] See page 665 in regard to the question of pseudopurpuric acid and the constitution of the metal salts of the acid.

appeared as the result of a condensation of an amine, uramil, with a ketone, alloxan, to form a " ketone ammonia" which by subsequent loss of water produces the imide (II.) :

$$CO—NH—CO—NH—CO—CH—NH_2 +$$

$$CO—CO—NH—CO—NH—CO \rightarrow$$

$$CO—NH—CO—NH—CO.CH—NH—$$

$$C(OH)—CO—NH—CO—NH—CO.$$

III.[1]
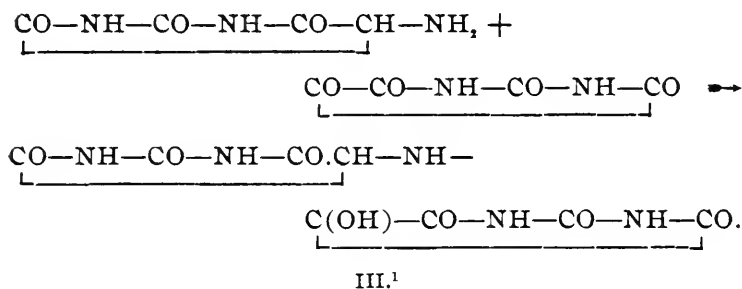
Especially the most striking property of purpuric acid, its great instability towards aqueous acids, is well expressed by the above formula. Imides, such as the imidoethers and imidoquinones, are well known to be readily saponified by aqueous acids. As purpuric acid is itself a fairly strong acid, its instability in the free state in the presence of water follows as a matter of course.[2] As will be shown presently, we have been able to prove conclusively that Beilstein's constitution (I.) for purpuric acid is wrong, and that murexide as dried at 100° is really the ammonium salt of an acid whose constitution is expressed in (II.). The interesting discovery was, moreover, made that there is a marked tendency for the condensation between uramil and alloxan to stop at the intermediate carbonyl ammonia stage (III.) and that freshly prepared murexide contains 1 molecule of water, which it loses at 100°. That this molecule of water is not water of crystallization but water used to form the carbonyl ammonia group was shown by the fact that it was possible to prepare salts of intensely colored derivatives of purpuric acid from γ-alkyluramils and alloxan ; for instance, in the presence of ammonia, salts were obtained by the following condensation :

[1] Bernthsen's "Lehrbuch" gives III. as a possible constitution for purpuric acid.
[2] Attempts will be made to isolate free purpuric acid in the absence of water and experiments made on the nature of the substances in aqueous solution formed immediately after the addition of an acid to a purpurate. J. Stieglitz.

$$\mathrm{CO-NH-CO-NH-CO-CH.(NHCH_3)} +$$

$$\mathrm{CO-CO-NH-CO-NH-CO} \longrightarrow$$

$$\mathrm{CO-NH-CO-NH-CO-CH-N(CH_3)-}$$

$$\mathrm{C(OH)-CO-NH-CO-NH-CO.}$$
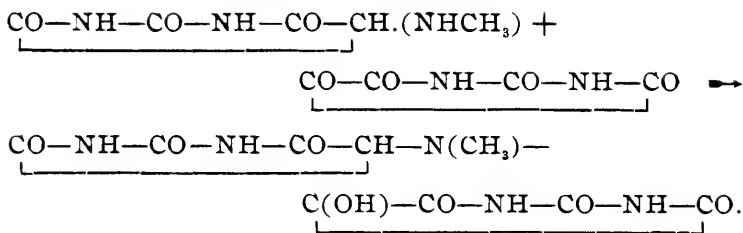
IV.

These substances cannot lose the molecule of water in question, but otherwise they resemble the purpurates, notably as regards intensity of color and sensitiveness to acids. This tendency to form carbonyl-ammonia derivatives is in perfect accord with the general behavior shown by mesoxalic acid and mesoxalylurea (alloxan) in forming stable hydrates of the carbonyl group, $: C(OH)_2$. It is probably owing to this tendency, too, that purpuric acid shows such extreme sensitiveness to acids, for it is well known that carbonyl ammonias, like aldehyde ammonias, are even more rapidly decomposed by acids than imido compounds are hydrolyzed.

The proof that the true constitution of purpuric acid is represented by II.[1] (respectively III. for the hydrate) and not by I. is based on the following lines of experiment :

1. Constitution I. represents a symmetrical molecule; the same ammonium salt of 1,3-dimethylpurpuric acid ought to result on condensing either 1,3-dimethyluramil with alloxan or uramil with 1,3-dimethylalloxan, if Beilstein's constitution is correct. II. and III. are unsymmetrical and enable us to predict that the ammonium salts of two isomeric dimethyl-purpuric acids (1,3 and 1',3') would result from the above condensations. Our experiments show that two isomers are actually obtained.

2. According to II. (and III.) the presence of the hydrogen attached to the carbon atom, 5, of the uramil group is not essential for the formation of condensation-products of the nature of purpuric acid, while according to Beilstein's formula it is. We have found that 5-amido-6-methyl uracil

[1] II. and III. are " pseudo" purpuric acids as will be explained further on.

condenses with alloxan to form a deep-red compound of the general character and composition of the purpurates; the uracil has the amine group attached to a tertiary carbon atom holding no hydrogen.

3. The purpurate obtained from 7-methyluramil and alloxan in ammoniacal solution has the composition $C_9H_{12}O_7N_6$, even when dried at 100°, as required by constitution III. There is no tendency shown to lose water to form a triatomic ring as required by I., even when there is no opportunity to lose water to form an imide according to II.

We may therefore consider the evidence as conclusive that II. and not I. represents the constitution of purpuric acid and its anhydrous salts, as far as the linking of the carbon, nitrogen, and oxygen atoms is concerned, and that III. represents the constitution of the hydrated salts.

We have also begun an investigation of the interesting question as to which hydrogen atom in purpuric acid is involved in the formation of its monobasic salts and particularly as to the constitution of these salts. The evidence points to the conclusion that the more ionizable hydrogen is the one in position 5 of the uramil ring, and that in the salts the metal is bound, as we expected, to the oxygen of the neighboring carbonyl group (4 or 6). We have then for the constitution of murexide in its anhydrous form :

$$\begin{array}{ccccccc}
NH\!\!-\!\!-CO & & & & CO\!\!-\!\!-NH \\
| & | & & & | & | \\
CO & C\!\!-\!\!-\!\!-\!\!N\!\!=\!\!=\!\!=\!\!C & CO\,. \\
| & \| & & & | & | \\
NH\!\!-\!\!-C(ONH_4) & & & & CO\!\!-\!\!-NH
\end{array}$$

V.
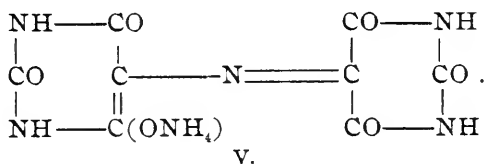
Whether purpuric acid in the free state would exist in the pseudo form II. (respectively III.), as is likely, or as the true acid corresponding to V. is a question which can only be answered when the acid has been isolated. The proof that the metal is attached to oxygen in the purpurates rests on the fact that silver purpurate, when treated with methyl iodide, produces a methyl ether which with dry hydrogen chloride at 125° to 130° gives a large quantity of methyl chloride. As is

well known, this is a characteristic reaction of a methoxyl group, —OCH$_3$; under the conditions named, neither methylimide groups nor methylcarbin groups, : C—(CH$_3$), would lose methyl chloride. That we are justified in concluding that the metal is bound to oxygen from the formation of an oxygen ether from the silver salt follows from the work of Nef[1] on the salts of malonic and acetoacetic esters, from various investigations on the silver salts of acylamides,[2] and from the work of Hantzsch[3] on pseudo-acids and their salts, work which by physico-chemical determinations fully established the conclusions based in the previous investigations on synthetic results. They all agree in showing that silver salts produce oxygen ethers when the salts hold the metals attached to oxygen.

Sodium and potassium salts, on the other hand, while having the same constitution as the silver salts, *i, e.*, holding the metal attached to oxygen,[4] are known to give as a rule with methyl iodide methyl derivatives of the tautomeric or pseudoform of the acid,[5] and this fact is very valuable in determining whence the ionizable hydrogen of the true acid is obtained. Applying this method to the purpurates we have found that potassium purpurate, when treated with methyl iodide, produces a methyl derivative from which hydrogen chloride does not split off methyl chloride, and from which by destructive treatment with concentrated aqueous hydrochloric acid no methylamine could be obtained. It is almost certain, therefore, that the methyl group has gone into position 5 of the uramil half of purpuric acid and that, consequently, it is the hydrogen atom in this position of the pseudo-acid, which is used to form with either of the (identical) neighboring car-

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[1] Ann. Chem. (Liebig), **266**, 66 (1891) ; **276**, 235 (1893).

[2] Tafel and Enoch : Ber. d. chem. Ges., **23**, 104 and 1550 (1890) ; Comstock and Kleeberg : This JOURNAL, **12**, 493 (1890) ; Comstock and Wheeler : *Ibid.*, **13**, 520 (1891) ; Stieglitz and Dains : J. Am. Chem. Soc., **21**, 187 (1899).

[3] Ber. d. chem. Ges., **32**, 575 (1899).

[4] This is proved conclusively by Hantzsch, *Loc. cit.*

[5] This is so in all of the cases quoted above. The reaction is analogous to the fact established by Wheeler that imidoethers, of the formula RC(: NH)OCH$_3$, which correspond to the salts, RC(: NH)OK, give with methyl iodide acylmethylamines, RCO.NHCH$_3$. It is probable that methyl derivatives of the pseudo-acids would result from the treatment with methyl iodide of all oxygen ethers of the corresponding true acids, the former being the more stable compounds.

bonyl groups the true acid group : C(OH). We shall endeavor to confirm this conclusion by determining whether alanine, $CH_3CH(NH_2)CO_2H$, is formed by decomposition of the product. The same conclusion as to the hydrogen atom of purpuric acid which is taken to form the metal salts (V.) follows indirectly from the fact that 1,3-dimethylalloxan and 1,3-dimethyluramil condense to form 1,3,1′,3′-tetramethyl-purpurates (murexoin).

We suspect that the change of structure from the pseudo-form, II. or III., to that of the salts, V, may have an important connection with the question of color in this group. The following compounds which have a structure corresponding to V. are intensely colored : 1. The purpurates like murexide. 2. The oxygen ester of purpuric acid as obtained from the silver salt and methyl iodide. 3. The salts of 7-alkylpurpuric acids. 4. The condensation-product of 4-methyl-6-amino-uracil and alloxan. On the other hand, the product obtained by methylation of the potassium salt of purpuric acid is pale-yellow, and, as we have just seen, it is most likely-5-methylpurpuric acid, a derivative of the pseudo-form, II. Alloxantin, which, as we shall presently show, almost surely has a constitution entirely analogous to the pseudo-form, III., is also colorless. It is possible, therefore, that purpuric acid itself will be found to be colorless, should it be more stable in the pseudo-form, II., than in the acid form, V. The residue left when methyl purpurate (the red oxygen ether) is treated with dry hydrogen chloride at 130° is white and gives instantly a deep-red solution on being treated with ammonia ; the white substance is most likely pseudopurpuric acid, II., itself, but further investigation will be necessary before we can speak authoritatively on this point or the question of color in this group, and we wish to reserve the field for further development in this laboratory.[1]

Another condensation-product of alloxan that is closely related to murexide is alloxantin. Formed by the condensation of alloxan with dialuric acid (tartronylurea), it can also be prepared by the reduction of alloxan by means of hydrogen sulphide. Unlike purpuric acid, it is stable only in acid

[1] Mr. R. W. Noble is continuing the investigation under the direction of one of us.

solutions, alkalies decomposing it at once into salts of dialuric acid and alloxan. Its seemingly close relation to purpuric acid is shown by its easy conversion into murexide through the action of ammonia. This and its formation by the reduction of alloxan has been expressed by the following constitution which has commonly been accepted :

$$CO—NH—CO—NH—CO—C(OH)—$$
$$C(OH)—CO—NH—CO—NH—CO. \quad VI.$$
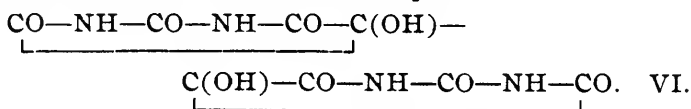
Its sensitiveness to alkalies and its relation to purpuric acid suggest the following constitution :

$$CO—NH—CO—NH—CO—CH—O—$$
$$C(OH)—CO—NH—CO—NH—CO. \quad VII.$$
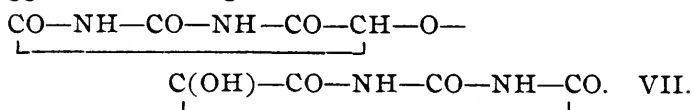
According to this view it would appear as the hemi-acetal of the alcohol (or phenol), tartronylurea, and the ketone, mesoxalylurea. Such an acetal would readily form with ammonia uramil and alloxan, which would then condense in the presence of an excess of ammonia to murexide. With bases it would give dialurates and salts of alloxan. The existence of tetramethylalloxantin (amilinic acid) and its conversion into tetramethylmurexide through the action of ammonia reduces the question of the constitution of alloxantin to the determination of the function of the hydrogen atoms in the tartronyl radical. The constitution of purpuric acid having been determined, the investigation will be extended to bring more rigorous proof of the correctness of the constitution VII., suggested for alloxantin.

EXPERIMENTAL PART.

The Asymmetry of the Purpuric Acid Molecule.

Ammonium 1,3-Dimethylpurpurate,
$$CO.NCH_3.CO.NCH_3.C(ONH_4):C—N:C.CO.NH.CO.NH.CO,$$

and Ammonium 1',3'-Dimethylpurpurate,
$$CO.NH.CONH.C(ONH_4):C—N:C.CO.NCH_3.CO.NCH_3.CO.$$
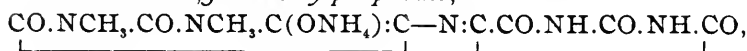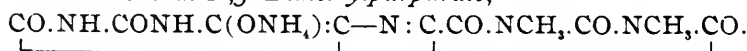
—Eight grams of 1,3-dimethyluramil, prepared from caffeine

according to Fisher's modification of Techow's method,[1] were added to 40 cc. of boiled water at the temperature of 70°, a stream of hydrogen being run through the flask to replace the air. Sufficient ammonium carbonate was now added to dissolve the uramil and the mixture added to 7 grams (1 molecule = 6.65 grams) of alloxan dissolved in 5 cc. of hot water. After the mixture was allowed to stand in the cold for half an hour, the crystals were filtered off and recrystallized from hot water. Yield, 9 grams.

For analysis the substance was dried at 100°.

0.1938 gram substance gave 0.0517 gram N.

0.2348 gram substance gave 0.3297 gram CO_2 and 0.0795 gram H_2O.

	Calculated for $C_{10}H_{12}O_6N_6$.	Found.
C	38.46	38.30
H	3.85	3.79
N	26.92	26.71

The substance crystallized in small, four-sided prisms, very similar to the ordinary murexide only a little yellower in luster.

Eight and five-tenths grams of the above compound (1,3-dimethylpurpurate of ammonium) were suspended in 30 cc. of water and the air in the flask replaced by hydrogen. The mixture was now made slightly acid with hydrochloric acid and warmed to 70° until it was of a pale-yellow color. After the mixture was cooled to 0°, the precipitate was filtered off, washed with a little cold water, and dried in a vacuum over sulphuric acid. Yield, 2.41 grams. Analysis showed that the body is dimethyluramil :[2]

0.4880 gram substance gave 0.1180 gram N.

[1] Ber. d. chem. Ges., **28**, 2475 (1895).

[2] In order to avoid repetition we wish to remark here that the bodies described in this paper, almost without exception, have no sharp melting-point but decompose at higher temperatures without melting. The investigation was for this reason rendered more difficult as the bodies obtained in a reaction as well as the recovered starting material could only be identified by analysis. Carbon and hydrogen were determined according to Dennstedt (Ztschr. anal. Chem., **41**, 525 (1902)). The nitrogen was determined according to Kjeldahl or by distillation with soda-lime, the strength of the acid used having been determined in terms of milligrams of nitrogen.

	Calculated for $C_4H_9O_2N_3$.	Found.
N	24.56	24.19

The filtrate and washings were now made more strongly acid and treated with hydrogen sulphide. There were obtained in this way 3.7 grams of alloxantin. After drying over sulphuric acid it gave the following analysis:

0.3172 gram substance gave 0.0557 gram N.

	Calculated for $C_8H_6O_8N_4 + 2H_2O$.	Found.
N	17.39	17.53

Treated with hydrochloric acid (sp. gr. 1.19) for five hours at 160°, it was completely decomposed, and after evaporation of the excess of acid and distillation with caustic potash, the distillate gave no test for methylamine.

In the same way uramil was condensed with dimethylalloxan to give another purpurate of ammonia (1′,3′-dimethylpurpurate of ammonia). This was so similar to its isomer in solubility and general appearance that had it not given other products on treatment with acids, it might have been taken to be identical with it.

Seven grams decomposed by the action of dilute hydrochloric acid gave a uramil which, on account of its difficult solubility, was at once recognized as ordinary dialuric acid amide. To further characterize the same it was also decomposed with strong hydrochloric acid as described above and tested for methylamine. With chloroform and caustic potash it did not give the faintest odor of methyl isocyanide.

From the mother-liquid there was thrown out by the action of hydrogen sulphide a white crystalline solid which on recrystallization from hot water proved, on analysis, to be amilinic acid (tetramethylalloxantin). For analysis the same was dried at 100°.

0.2183 gram substance gave 0.3354 gram CO_2 and 0.0783 gram H_2O.

0.2990 gram substance gave 0.0477 gram N.

	Calculated for $C_{12}H_{14}O_9N_4$.	Found.
C	42.10	41.90
H	4.09	4.01
N	16.37	15.96

The above experiments show conclusively that the molecule of purpuric acid is not symmetrical, for the two acids obtained above are different, as shown by their having different decomposition-products.

The Condensation of 5-Amido-4-methyluracil with Alloxan.

4-*Methyluracilimidoalloxan,*
CO.NH.CONHC(CH$_3$) : C—N=C.CONHCONHCO.—Four
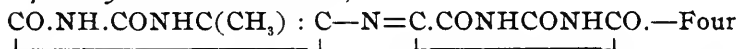
grams of the uracil[1] were placed in a flask with 4 grams of alloxan, and, after the addition of 25 cc. of water, were heated on the water-bath for twenty minutes. The mixture soon became a deep wine-red color and after the addition of 50 cc. of strong alcohol and cooling deposited a heavy, dark-red precipitate. This product could not be obtained in well-defined crystals; the analysis proves that the product has the composition $C_9H_7O_5N_5$. For analysis it was dried at 100°.

0.2359 gram substance gave 0.3453 gram CO_2 and 0.0544 gram H_2O.

0.2866 gram substance gave 0.0769 gram N.

	Calculated for $C_9H_7O_5N_5$.	Found.
C	40.07	39.92
H	2.64	2.58
N	26.41	26.84

In amidomethyluracil the amido group is attached to a tertiary carbon atom. That it forms a murexide-like condensation-product with alloxan is good evidence of the incorrectness of Beilstein's formula.

The Action of Ammonia and Primary Amines on Alloxantin and the Significance of the Water of Crystallization in the Salts of Purpuric Acid.

Gmelin[2] first prepared murexide by heating alloxantin in a

[1] Behrend : Ann. Chem. (Liebig), **231**, 250 (1885).
[2] Gmelin, V., 326.

stream of dry ammonia gas at 100° and recommends this as
the best method of preparing the same. Later Rochleder[1]
prepared murexoin (tetramethylpurpurate of ammonia) in the
same way. We used the method a number of times for pre-
paring murexide and found that it gave very good yields if
absolute purity was not desired. In order to remove the last
traces of alloxantin frequent recrystallization is, however,
necessary, and much loss of material results. The following
improvement of Gmelin's method which gives quantitative
yields of almost pure material can be highly recommended :

Twenty grams of finely powdered and dried alloxantin are
placed in a large tube and after the addition of 2 gram-mole-
cules of ammonia dissolved in 100 cc. of absolute alcohol, the
tube is sealed and heated to 100° for ten hours, being shaken
from time to time. At the end of this time the alloxantin is
completely converted into anhydrous murexide. It need only
be filtered from the mother-liquid and washed with a little
alcohol and it is then perfectly pure. Yield, about 20 grams.

When examined in the light of the formula that we have
proposed for alloxantin the mechanism of this reaction is very
simple. Alloxantin, the dialuric acid ester of alloxan, gives
with ammonia the acid amide, uramil, and alloxan ; these
then condense in the presence of a second molecule of ammo-
nia, giving purpurate of ammonia. This tendency of alloxan-
tin to react with amines has long been known but a plausible
explanation has never been offered before. For instance,
boiled with ammonium chloride it gives uramil, alloxan, and
hydrochloric acid ;[2] in the same way, boiling it with cyanamide
converts it into pseudouric acid and alloxan.[3] In a later
paper this very fruitful reaction will be more carefully treated
and some of the simpler esters of dialuric acid as well as the
synthesis of dialuric acid amides (uramils) and ureids (pseudo-
uric acids) more fully described.

Beilstein and the older chemists who have analyzed the
salts of purpuric acid, dried the same at 100°, and found that
they were anhydrous with the exception of the silver salt

[1] Jsb., 1850, p. 436. See also Brunn : Ber. d. chem. Ges., **21**, 514 (1888).

[2] Mulder : Ber. d. chem. Ges., **6**, 1235 (1873).

[3] Mulder : *Ibid.*, **6**, 1236 (1873).

which has 0.5 molecule of water. Matignon[1] first described murexide as containing 1 molecule of water, which it loses already below 100°. We have again analyzed a number of purpurates and find that they all, when freshly prepared, contain 1 molecule of water, which they lose at ordinary temperature on standing.

Ammonium purpurate hydrate, prepared as described above and recrystallized from water containing a few drops of ammonia, was spread on a clay plate for twenty minutes at room temperature and analyzed :

0.2711 gram substance gave 0.3164 gram CO_2 and 0.0786 gram H_2O.

0.4247 gram substance gave 0.1195 gram N.

	Calculated for $C_8H_{10}O_7N_6$.	Found.
C	31.78	31.83
H	3.31	3.24
N	27.81	28.14

Potassium purpurate hydrate, prepared as described below, was dried in the same way and analyzed as follows :

0.5873 gram substance gave 0.1653 gram K_2SO_4.

	Calculated for $C_3H_6O_7N_5 \cdot K$.	Found.
K	12.38	12.64

The so-called water of crystallization present in the salts of purpuric acid is constitutional (see the introduction) and has the same significance as has the water in chloralhydroxylamine, which is also lost at ordinary temperature when that body goes over into chloraloxime. The group of purpuric acids that can be prepared from primary amines and alloxantin, that is, the condensation-products of alloxan and 7-alkyluramils, cannot lose water and have no water that could be mistaken for water of crystallization. Of this group the 7-methyl and the 7-ethylpurpurates of ammonia were prepared.

[1] Ann. chim. phys. [6], **28**, 346 (1893). He gives no analytical data in support of his views.

Ammonium 7-Methylpurpurate Hydrate,

$CO.NH.CO.NH.C(ONH_4):C—$

$(NCH_3).C(OH)CONHCONH.CO.—$
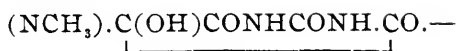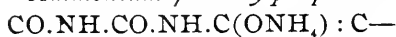
This body was prepared in a number of ways :

1. By the condensation of 7-methyluramil and alloxan.

7-Methyluramil was prepared by the action of methylamine sulphite on alloxan as recommended by Fischer.[1] We worked at a much lower temperature than Fischer did and used pure methylamine, but even then did not get a perfectly pure product, as was shown by its analysis and by its reaction with potassium cyanate, which gave some pseudouric acid. The formation of a slight amount of ordinary uramil is easily explained on the assumption that the methylamine decomposed some of the alloxan with the formation of ammonia. For analysis it was dried at 100°.

0.2785 gram substance gave 0.3864 gram CO_2 and 0.1023 gram H_2O.

0.4731 gram substance gave 0.1282 gram N.

	Calculated for $C_5H_7O_3N_3$.	Found.
C	38.21	37.84
H	4.45	4.10
N	26.75	27.12

Absolutely pure *7-methyluramil* can be obtained by the action of methylamine at low temperatures on alloxantin or other esters of dialuric acid. Some prepared in this way was analyzed as follows :

0.2034 gram substance gave 0.2839 gram CO_2 and 0.0794 gram H_2O.

0.3390 gram substance gave 0.0905 gram N.

	Calculated for $C_5H_7O_3N_3$.	Found.
C	38.21	38.07
H	4.45	4.36
N	26.75	26.62

Four grams of 7-methyluramil were dissolved in a little

[1] Ber. d. chem. Ges., **30**, 561 (1897).

more than 1 molecule of aqueous ammonia (30 cc.) and the solution added to a solution of 3.6 grams of alloxan in 20 cc. of water. After the mixture was warmed for five minutes on the water-bath, some ammonium carbonate was added to aid crystallization and the mixture allowed to cool. Yield 3.1 grams. The body crystallized in small, four-sided prisms, which resembled the ordinary murexide so closely that they could only be distinguished by analysis. For analysis the body was dried at 100° :

0.2103 gram substance gave 0.2609 gram CO_2 and 0.0719 gram H_2O.

0.4181 gram substance gave 0.1105 gram N.

	Calculated for $C_9H_{12}O_7N_6$.	Found.
C	34.17	33.83
H	3.80	3.84
N	26.58	26.41

2. By the oxidation of 7-methyluramil with mercuric oxide.

Five grams of methyluramil and 4.5 grams of mercuric oxide were suspended in 100 cc. of water and the mixture heated to boiling. As the filtrate could not be made to crystallize on account of the great solubility of the methylammonium salt of methylpurpuric acid, 15 grams of ammonium carbonate were added. A heavy precipitate of the ammonium salt was formed. Yield, 2.3 grams.

0.3329 gram substance gave 0.0876 gram N.

	Calculated for $C_9H_{12}O_7N_6$.	Found.
N	26.58	26.32

3. The action of methylamine on alloxantin.

Fifteen grams of powdered and dried alloxantin were sealed into a glass tube with 100 cc. of absolute alcohol and 2 molecules of methylamine. After standing at room temperature for twenty-four hours the mixture was heated for five hours to 100°. Fourteen and eight-tenths grams of a dark-red solid were obtained, but on account of the great solubility of this methylammonium salt and because some decomposition had taken place, it could not be obtained sufficiently pure for

analysis. The body was therefore converted into the ammonium salt as follows : Ten grams of the solid were dissolved in 50 cc. of hot water and 1.5 grams of alloxan added. After the addition of 15 grams of ammonium carbonate the ammonium salt fell out as a mass of brilliant, greenish crystals. Yield, 7.3 grams.

Ammonium 7-Ethylpurpurate Hydrate,

$$CONHCONH.C(ONH_4):C.NC_2H_5.C(OH).CONHCONHCO.$$
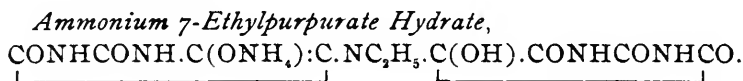
—7-Ethylpurpurate of ammonia was prepared from alloxantin and ethylamine in the same way as the above methyl compound. It was found, however, that the ethylamine acted on the alloxan formed, even more than did the methylamine. On this account it was found not advisable to use more than 1 molecule of ethylamine in the reaction. In this way the alloxantin was converted almost quantitatively into 7-ethyluramil and alloxan. Ten grams of alloxantin were suspended in 100 cc. of absolute alcohol and after the addition of 1 molecule of ethylamine, heated for seven hours to 100°. On opening the tube the solid contents were found to weigh 6.7 grams and in the alcohol were found 4.2 grams of alloxan. The 7-ethyluramil was at once converted into the corresponding purpurate of ammonia as follows : It was dissolved in 80 cc. of hot water and after the same had cooled to 70°, 5 grams of alloxan and 10 grams of powdered ammonium carbonate were added. On cooling, the ethylpurpurate of ammonia crystallized out. Yield, 6.23 grams. For analysis it was dried at 100°.

0.1978 gram substance gave 0.2621 gram CO_2 and 0.0760 gram H_2O.

0.3113 gram substance gave 0.0810 gram N.

	Calculated for $C_{10}H_{14}O_7N_6$.	Found.
C	36.36	36.15
H	4.24	4.30
N	25.45	26.01

The body resembles the other purpurates so closely that only the analysis and the decomposition-products can be used

as a means of identification. Treated with acids, it gives
7-ethyluramil. This body, which is even more soluble than
the methyl body, will be described at greater length in a later
paper.

The Position of the Metal in the Salts of Purpuric Acid.

Purpuric acid forms only one series of well-defined salts,
acting in this respect like a monobasic acid. The potassium
and silver salts were methylated in order to get some idea as
to the position of the metal in them.

The potassium salt of purpuric acid has been prepared by
boiling murexide with a large excess of potassium chloride.
This method does not give a very pure product unless the
same is frequently recrystallized with great loss of material.
We can recommend the following method of condensing ura-
mil and alloxan in the presence of caustic potash as giving
good yields of very pure salt.

The uramil used in this and the other experiments was
made from malonic ester. The same was converted into bar-
bituric acid by a modification of Michael's method.[1] We be-
believe that the method as described by Michael will not give
over 40 per cent to 50 per cent yields. In the same way Tafel
and Weinschenk[2] were unable to obtain more than 40 per cent
by their modification of the same method. By working at
slightly higher temperatures and under pressure we found
that one obtains almost a quantitative yield.

Four and six-tenths grams of metallic sodium are dissolved
in 100 cc. of absolute alcohol and to the hot solution 12 grams
of powdered urea are quickly added. In the mean time one
has prepared a solution of 32 grams of malonic ester in 50 cc.
of alcohol and, as soon as the urea is all dissolved, the two
solutions are rapidly mixed and poured into a large tube or
pressure-bottle and sealed up. The mixture becomes thick at
once, and if it is heated to 100° for seven hours the reaction is
found to be complete. The tube is now opened and the con-

[1] J. prakt. Chem., **35**, 456.
[2] Ber. d. chem. Ges., **33**, 3383 (1890).

tents are dissolved in the least amount of hot water and decomposed with acids.[1] Yield, 94 to 97 per cent.

The barbituric acid was converted into potassium violurate by means of potassium nitrite and acetic acid and the violurate reduced to uramil by hydriodic acid and phosphonium iodide. We obtained in this way 70 per cent of the malonic ester converted into uramil. To convert the same into potassium purpurate it was dissolved in one gram-molecule of caustic potash in fifty times its weight of water, the air being replaced by a stream of hydrogen. When it had all dissolved, which sometimes required heating, the warm solution was poured into a solution of alloxan in ten times its weight of water. The solution of alloxan must not be poured into the alkaline solution of uramil as the free alkali then decomposes the purpurate formed.

5-Methylpurpuric Acid,

$$\text{CO.NH.CO.NH.CO.C(CH}_3\text{).N : C.CO.NH.CO.NH.CO.} \text{---}$$
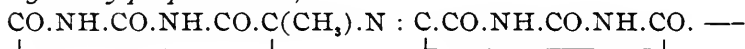
The potassium salt was dried at 100° and methylated by being heated to 100° for five hours with one gram-molecule of methyl iodide diluted with an equal volume of absolute ether. The tube was now opened and the solid filtered off and a portion recrystallized from water and analyzed :[2]

0.2121 gram substance gave 0.2965 gram CO_2 and 0.0485 gram H_2O.

0.3172 gram substance gave 0.0802 gram N.

	Calculated for $C_9H_7O_6N_5$.	Found.
C	38.43	38.12
H	2.49	2.57
N	24.91	25.27

[1] Monomethylbarbituric acid was prepared in the same way. As starting material we used the mixture obtained on methylating malonic ester with methyl iodide according to Conrad. This contains only about 80 per cent of monomethylmalonic ester together with unchanged ester and some dimethyl ester. The yield of pure material after recrystallizing from water was 17.2 grams out of 35 grams of mixed esters or calculated for the monomethyl ester, 80 per cent of the theory. It possessed the crystal form and other properties ascribed to it by Franchimont and Klobbie, but melted at 202° (corr.), 10° higher than found by these investigators.

[2] The methyl ether as prepared was pale-yellow, but on recrystallizing became red. This may have been due to some decomposition, and as it is of importance in view of the theory that we have proposed for the color of these bodies, we shall try to prepare 5-methyluramil and condense it with alloxan.

O-4-Methyl purpurate,
CO.NHCONHC(OCH₃) : C.N : C.CO.NH.CO.NH.CO. —
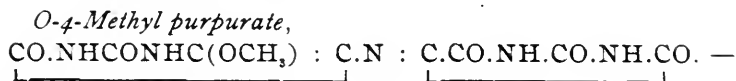
Silver purpurate, prepared by the precipitation of a solution of murexide with silver nitrate, was dried at 100° and then heated to 100 for three hours with 1 gram-molecule of methyl iodide and the same volume of absolute ether. The tube was now opened and the mixture of silver iodide and the methyl ether filtered off. Attempts to purify the ether by recrystallization from water or alcohol failed on account of the great instability of the body. It is slowly hydrolyzed even by boiling water.

0.174 gram of silver purpurate that had been dried at 100° were methylated as above and the product carefully collected and placed in a small flask which was connected with an azotometer filled with strong caustic potash. After the air had been expelled from the apparatus by means of carbon dioxide, dry hydrogen chloride was passed through, the flask being heated in an oil-bath. At 125° to 130° a gas, methyl chloride, was given off which was not absorbed by caustic potash and which burned, on being ignited, with a lambent green flame. The theory demanded 14 cc. of gas; there were obtained 6.8 cc.

In view of the fact that methyl chloride is quite soluble in water, the above experiment would tend to show that when the silver salt of purpuric acid is methylated the oxygen ether is formed. The body is colored very deep red but on being dissolved in hot water as described above, it is rapidly hydrolyzed and forms a colorless solution.

The work on the salts of purpuric acids will be continued. Special stress is to be laid on the cause of color in this group and on the question of the existence of free purpuric acid.

CHICAGO, March 10, 1903.

NOTE.

To the Editor :

In the March[1] issue of your JOURNAL was published an article about '' The Action of Ammonia upon Copper Sulphate Solutions,'' by James Locke and the undersigned. I have worked out the experimental part of the investigation, but I wish to state that I am not responsible for the theoretical speculations advanced in the article, this not being referred to me before printing. Very respectfully,

JACOB FORSSELL.

REVIEWS.

DIE WISSENSCHAFT. Sammlung naturwissenschaftlicher und mathematischer Monographien. Heft 1.

UNTERSUCHUNGEN ÜBER DIE RADIOAKTIVEN SUBSTANZEN. Von MME. CURIE. Uebersetzt und mit Literatur-Ergänzungen versehen von W. KAUFMANN. Mit eingedruckten Abbildungen. Braunschweig : Druck und Verlag von Friedrich Vieweg und Sohn. 8vo. 1904. pp. viii + 132. Price, 3 marks.

The publishers of this little volume announce that they propose to issue from time to time similar monographs on various subjects dealing with the natural sciences and mathematics. The treatment is not to be popular in the ordinary sense of the word, but the monographs will be intended for specialists and will therefore give some of the experimental and theoretical methods that have been adopted by investigators. This volume will be welcomed by physicists and chemists the world over. It brings together in clear form the principal results of the investigations upon the subject of radio-active substances which have hitherto been published. It is essentially the dissertation of Mme. Curie. The author has, however, not confined herself wholly to her own work, but has embodied all important investigations that have been carried out up to the latter part of 1903. Every one interested in the subject of radioactivity should have a copy of this book. It need scarcely be said that the treatment is clear and interesting. I. R.

PHYSICAL CHEMISTRY IN THE SERVICE OF THE SCIENCES. By JACOBUS H. VAN 'T HOFF, Member of the Prussian Academy of Sciences, Professor Ordinarius, Honorarius in the University of Berlin. English version by ALEXANDER SMITH, of the Department of Chemistry, University of Chicago. University of Chicago Press. 1903.

As is well known, Prof. van't Hoff came to this country and gave a brief course of lectures at the University of Chicago at

[1] This JOURNAL, 31, 268.

their decennial celebration. The present little volume contains an account of what he said. The first, or introductory lecture, discusses the rise of the new Physical Chemistry. The second and third lectures deal with the relations between Physical Chemistry and Pure Chemistry, and for the chemist are the most interesting part of the course. The great contributions of physical chemistry to chemistry in general are through the extension of Avogadro's law to solutions, through the applications of thermodynamics and through the theory of electrolytic dissociation.

Two lectures were devoted to the applications of Physical Chemistry to Industrial Chemistry, two to the relations between Physical Chemistry and Physiology, and two to the bearing of Physical Chemistry on Geology.

The lectures present in a clear and concise form some of the more important relations between physical chemistry and other branches of natural science, and will prove interesting reading to the chemist, physiologist, and geologist.

H. C. J.

A Short Hand-Book of Oil Analyses. By Augustus H. Gill, S.B., Ph.D. Third Edition, Revised and Enlarged. Philadelphia and London : J. B. Lippincott Company. 1903. pp. 158.

Dr. Gill has thoroughly revised the former editions and by the addition of a number of new methods brought the work up to date. The book is divided into two parts. In Part I., Physical and Chemical Tests, the author has included only the standard methods, and while he has described these in a most concise manner he has not omitted to call attention to their weaknesses and limits as to accuracy.

The petroleum products for lubricating and burning purposes are considered first and then the vegetable and animal oils, concluding with a short chapter on the method of examination of an unknown oil.

In Part II., Derivation, Description, and Examination of Certain Oils, the author has given in a very brief way the more important facts about the common oils as to their source, use, and probable adulterants.

The petroleum products are taken up first, giving a list of the various distillates and fractions with their commercial names, boiling-points, and specific gravities. Then the vegetable and animal oils are considered. The ordinary constants are given with a short discussion of their value in detection of adulteration.

In the appendix there are a number of valuable tables on flashing-points of oils and the various state and city regula-

tions. Comparison of viscosimeters, constants of various oils and fatty acids, and comparison of iodine numbers by the Hübl, Hanus, and Wijs methods are given, and also a list of reagents and how to prepare them. In closing, the specifica‐ tions are given for oils used by the Pennsylvania Railroad.

In the description of the Hanus method for iodine absorp‐ tion, the addition of 100 cc. of water before the titration has been omitted.

In a number of places the author has omitted to state whether Fahrenheit or Centigrade degrees are meant. In some cases there would be doubt in the mind of the student.

The Bömer method for the separation of phytosterol and cholesterol as given on page 86 is quite different from that given in his original article *Ztschr. Nahr. u. Genus.*, **1**, 38 (1898), and would hardly be satisfactory if used as directed.

These are, however, unimportant points. The author has certainly succeeded in collecting a very large amount of ac‐ curate information in a very small space, and the book, while especially fitted for the needs of the student of technical chem‐ istry, is very valuable as a source of ready reference in the laboratory of the oil analyst.   L. M. T.

FRACTIONAL DISTILLATION. By SYDNEY YOUNG, D.Sc., F.R.S., Pro‐ fessor of Chemistry in University College, Bristol. With 72 illus‐ trations. London : Macmillan & Co., Limited ; New York : The Macmillan Company. 8vo. 1903. pp. xii + 284.

Having been engaged for a number of years on investiga‐ tions in which it was necessary to use substances in a state of utmost purity, the author naturally resorted frequently to fractional distillation as a means of purification. This led to a familiarity with the methods and forms of apparatus devised by others, while new means were also invented to overcome special difficulties. '' It is in the hope that the solution of the difficulties which so often occur in carrying out a fractional distillation may be rendered easier, and that the value and economy of highly efficient still-heads in laboratory work may come to be more widely recognized than is generally the case at present, that this book is written.'' The whole subject is treated quite fully, having chapters on the apparatus used, including thermometer and barometer corrections, vapor pressures and boiling-points of mixed liquids, modifications of the still-head, mixtures of constant boiling-point, etc. The subject is treated both from the experimental and theoretical points of view, and the results and formulas of other workers are given, the references being placed at the end of each chap‐ ter. The chapters that are of most importance to chemists

generally are the three that discuss the modifications of the still-head. "Of all possible forms the plain vertical still-head is the least efficient," yet it is the one most frequently used in laboratories. Even it may have its efficiency increased by being made longer and narrower, although the limit is soon reached on account of the tendency of the condensed liquid in it to be hurled upward by the rising vapors. The simplest improvement is to slant the still-head. Not only is the efficiency increased, but the amount of liquid lost by adhering to the walls is decreased. A spiral still-head carries the idea, and also the efficiency a step further, and the amount of loss is even less, for a given length of tube. In general, it may be said that any of the well-known modifications of the still-head has greater efficiency than the form in common use. The one which, on the whole, is preferable, causes the ascending vapors to pass through the condensed liquid in the stem most frequently, and at the same time is the one in which least liquid remains at the end of the operation. The book is one that will repay careful reading on account of the many valuable suggestions contained in its pages. c. e. w.

TRAITÉ D'ANALYSE DES SUBSTANCES MINÉRALES. Par ADOLPHE CAR-
NOT, Membre de l'Institut, Directeur de l'École Supérieure des Mines. Tome second : Metalloïdes. Ch. Dunod, Éditeur, Paris. Grand in-8 de 821 pages, avec figures. 25 fr.

The first volume of this work explained the different methods in use for the qualitative examination and the quantitative analysis of mineral substances. The second volume is devoted to the analytical study of the metalloids, while the metals are to be treated in the two succeeding volumes. Among the metalloids are included not only those elements usually so classified, but also a number of rarer elements which are of a metallic nature, but whose properties and compounds strongly resemble those of undoubted non-metals. Among these are tungsten, vanadium, molybdenum, titanium, etc. In justification of this course it is pointed out that these elements modify the properties of iron, in particular, in much the same way as carbon, silicon, phosphorus, sulphur, etc.

Each element is taken up in a separate chapter, in which its occurrence, its properties and those of its principal compounds, and the chief reactions having an analytical bearing are given fully. The methods of separation and analysis are discussed in detail. Many of the subjects dealt with in this volume are of especial interest in industrial chemistry, agriculture, and hygiene. For instance, ammonia, nitric and nitrous acids, the hydrocarbons, mineral fuels, the cyanides, the halogens,

including bleaching agents, sulphides and sulphuric acid, phosphates, arsenic compounds, borates, natural and commercial silicates, the minerals and compounds of titanium, tungsten, molybdenum, etc. The book is one that must prove of value in chemical libraries. C. E. W.

KARL HEUMANN'S ANLEITUNG ZUM EXPERIMENTIEREN BEI VORLESUNGEN ÜBER ANORGANISCHEN CHEMIE, zum Gebrauch an Universitäten, technischen Hochschulen und höheren Lehranstalten. Von PROF. DR. O. KÜHLING. Dritte Auflage. Mit 404 in den Text eingedruckten Abbildungen. Braunschweig : Druck and Verlag von Friedrich Vieweg und Sohn. 1904. xxix + 818 Seiten.

The present edition of this well-known work on lecture experiments is not simply a reprint of the preceding edition, although nearly ten years have elapsed since the death of the original author. This could not be the case if the book was to be up to date, on account of the enormous development of inorganic chemistry along different lines, especially physical chemistry, electrochemistry, and numerous investigations at high and low temperatures. Most of the new experiments described illustrate the principles of electrochemistry, although the use of liquid air, the electric furnace, and the Goldschmidt process (indexed as " Aluminothermie") is not overlooked. The character of most physical-chemical experiments is such as to make them unsuitable for lecture demonstrations. The number would be still smaller if the lantern could not be used. This instrument has become so useful that the necessary electrical equipment for it, as well as for the furnace, receive considerable attention in this edition. Most teachers are satisfied with the books of Newth or Benedict, which contain more than enough material for the average course of lectures, but it is well to have at hand some larger work as a reference book. For this purpose there is probably none better than " Heumann." C. E. W.

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